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DEHYDRATION OF COBALT(II) CHLORIDE AND POTASSIUM TETRACHLOROCOBALTATE(II) HYDRATES

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DEHYDRATION OF COBALT(II) CHLORIDE AND POTASSIUM TETRACHLOROCOBALTATE(II) HYDRATES

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DEHYDRATION OF COBALT(II) CHLORIDE AND POTASSIUM TETRACHLOROCOBALTATE(II) HYDRATES

CHAPTER I

INTRODUCTION

Chemists, for many years, have been interested in the color changes that take place in cobalt(II) chloride during hydration. The changes from the blue $CoCl_2$ to the red $CoCl_2 \cdot 6H_2O$ have been used as a humidity indicator for many years to astound freshmen taking chemistry and to confound the uninitiated. Until lately, relatively little was understood about this process, and only now can we begin to explain what is happening.

The colors of solutions of $CoCl_2$ have been studied in an attempt to explain the changes caused by different ligands. The red color was finally assigned to six coordinate cobalt ions and the blue color to four coordinate ions. The blue $CoCl_4^{-2}$ ion, shown to be present in concentrated hydrochloric acid solutions of $CoCl_2$, agrees with this explanation. However, the blue color of $CoCl_2$ in ethyl alcohol, methyl

alcohol, and acetone cannot be explained by formation of $CoCl_4^{-2}$ and has been ascribed to compounds of the type CoL_2Cl_2 (where L= solvent molecule). It has been generally accepted that the pink-red aqueous solution is due to the $Co(H_2O)_6^{+2}$ ion.

Early experiments indicated that $CoCl_2.6H_2O$ loses four moles of water to form the violet $CoCl_2.2H_2O$ which then loses the remaining two moles of water to form anhydrous $CoCl_2$.[1] Later work has suggested the possibility of a tetrahydrate and a monohydrate. A trihydrate was indicated in an acetone-water mixture but was not isolated.[2]

The magnetic susceptibilities of the hexahydrate and anhydrous compounds have been measured with the hexahydrate showing a lower susceptibility but with the susceptibility of each compound well above the spin-only value expected from three unpaired electrons. This is consistent with other cobalt(II) compounds. It is suspected that at low temperatures these salts become antiferromagnetic. This has been shown for anhydrous $CoCl_2$[3] and also for the dihydrate.

The spectra of the hexahydrate, dihydrate, monohydrate, and anhydrous compounds have been measured.[4,5] It is generally agreed that all are octahedrally coordinated.

The crystal structures for $CoCl_2.6H_2O$, $CoCl_2.2H_2O$, and

$CoCl_2$ have been determined by x-ray crystallography. They have also shown octahedral coordination.

The goal of this work is to explain the structural changes which take place as water is lost from the hexahydrate by correlating the thermodynamic changes during the dehydration reactions with the changes in spectra and magnetic moments of the compounds. The theoretical basis lies in Crystal Field Theory by which the electronic spectra and magnetic moments can be calculated theoretically for different structures.

CHAPTER II

PREPARATION OF SAMPLES

Reagent grade cobalt(II) chloride hexahydrate was used as the starting material for each phase of the work. The hydrates containing fewer than six moles of water were prepared by placing a weighed sample of anhydrous $CoCl_2$ in a desiccator over wet calcium nitrate until the desired weight gain was obtained.

The anhydrous cobalt chloride was analyzed by dissolving a weighed sample in distilled water and gravimetrically determining the chloride ion concentration by precipitation as silver chloride. The hydrates were analyzed by complete dehydration and analysis of the anhydrous cobalt chloride formed. Sample weights varied from 0.100 to 0.500 grams. Analysis; calculated Cl^- = 54.61 %; found; 54.57 $\pm$ 0.07 %.

The hydrates were analyzed by studying the dissociation pressure as a function of the weight loss of the sample as discussed in chapter III. The weight loss was within 2 % of the theoretical weight loss in each case. The hydrates were

also analyzed by measuring the weight loss when a weighed sample of the hydrate was dehydrated. The weight loss was within 2 % of the theoretical value in each case.

For the magnetic susceptibility measurements, solutions of reagent grade cobalt chloride were purified by careful separation from iron and nickel impurities on a cation exchange column (Dowex 50W x 8. 50 - 100 mesh). The solid was then recrystallized from a concentrated acidic solution. The hydrates were prepared in the same way as before.

CHAPTER III

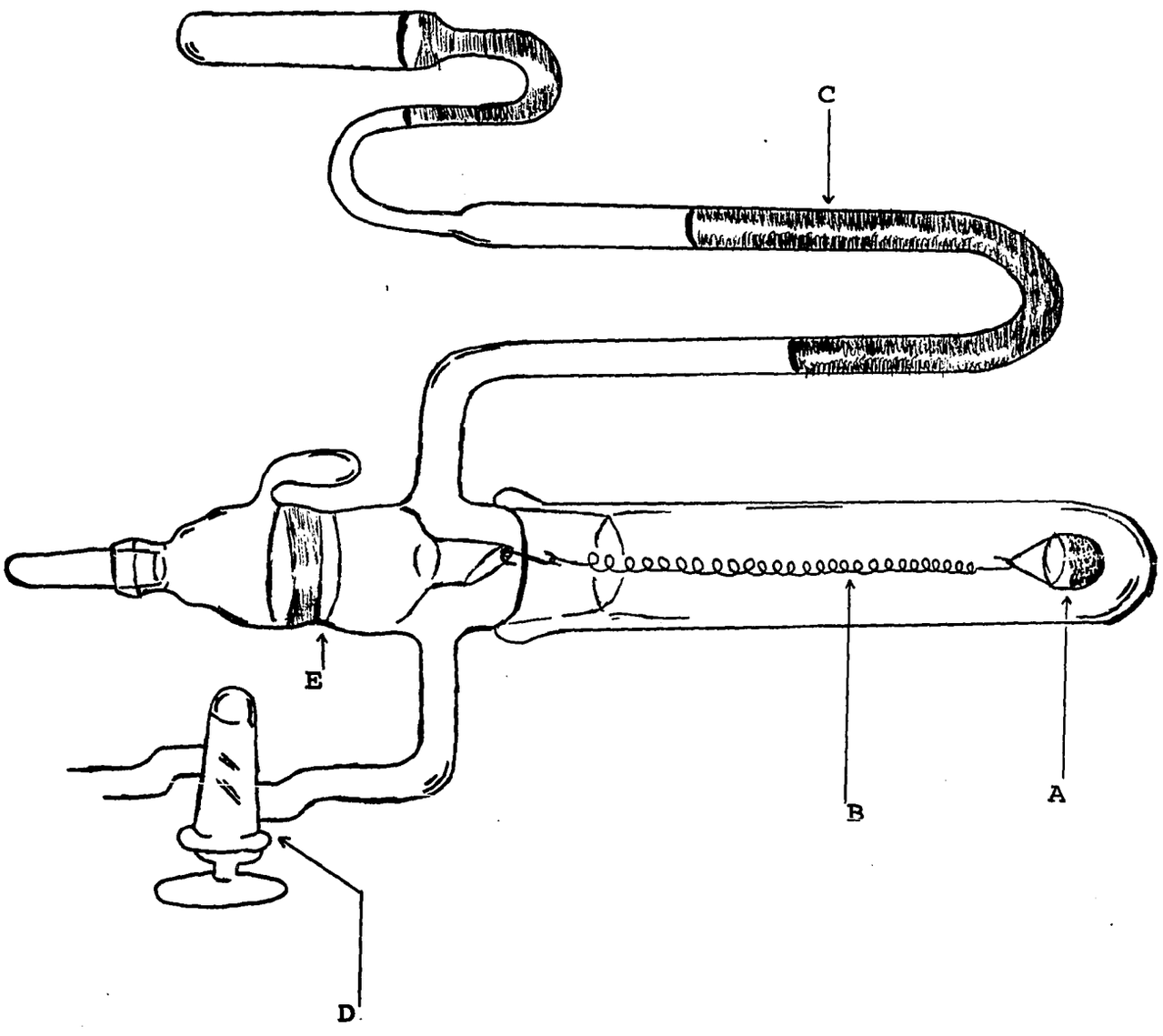
DISSOCIATION PRESSURES

Experimental

The dissociation pressures of the hydrates were studied as a function of composition and as a function of temperature.

The apparatus used is shown in figure 1. A weighed sample of the hydrate (A) was suspended from a calibrated quartz spring (with a capacity of 0.5 or 1.0 gram) (B) in a plastic bucket (or plastic lined aluminum bucket) inside a glass vacuum system. The system contained a manometer (C) for measuring the dissociation pressure, a vacuum stopcock (D) for evacuating water vapor, and a mercury sealed fritted disc (E) for the addition of water vapor to the system. During the lower temperature measurements, the entire system was submerged in a constant temperature bath. For the higher temperature work, only the sample chamber and sample were submerged in an oil bath equipped with a heating and temperature control system.

Figure 1



Apparatus for Dissociation Pressure Measurements

The dissociation pressures were studied as a function of composition by placing a sample of cobalt chloride hexahydrate in the vacuum system. With the temperature held constant (45^{o}), the system was allowed to equilibrate and the pressure was measured with a cathetometer. After equilibration and measurement, some water vapor was removed with a vacuum pump and the system was allowed to re-equilibrate. The amount of water loss was measured by measuring the change in the extention of the quartz spring with a cathetometer. A constant pressure plateau was obtained until the tetrahydrate was reached, and then a slight drop in pressure was observed. Another plateau was obtained until the dihydrate was reached. At the composition corresponding to the dihydrate, the dissociation pressure dropped to very low values; so the temperature was raised to 70^{o} C. At 70^{o} C a constant pressure plateau was obtained and the pressure dropped to near zero at the composition corresponding to the monohydrate. With the temperature raised to 110^{o} C, a fourth constant pressure plateau was obtained, and the pressure dropped to zero as the anhydrous $CoCl_2$ was formed.

The results are shown in figure 2.

The changes in dissociation pressure with respect to composition indicate the following series of dehydration reactions in vacuo:

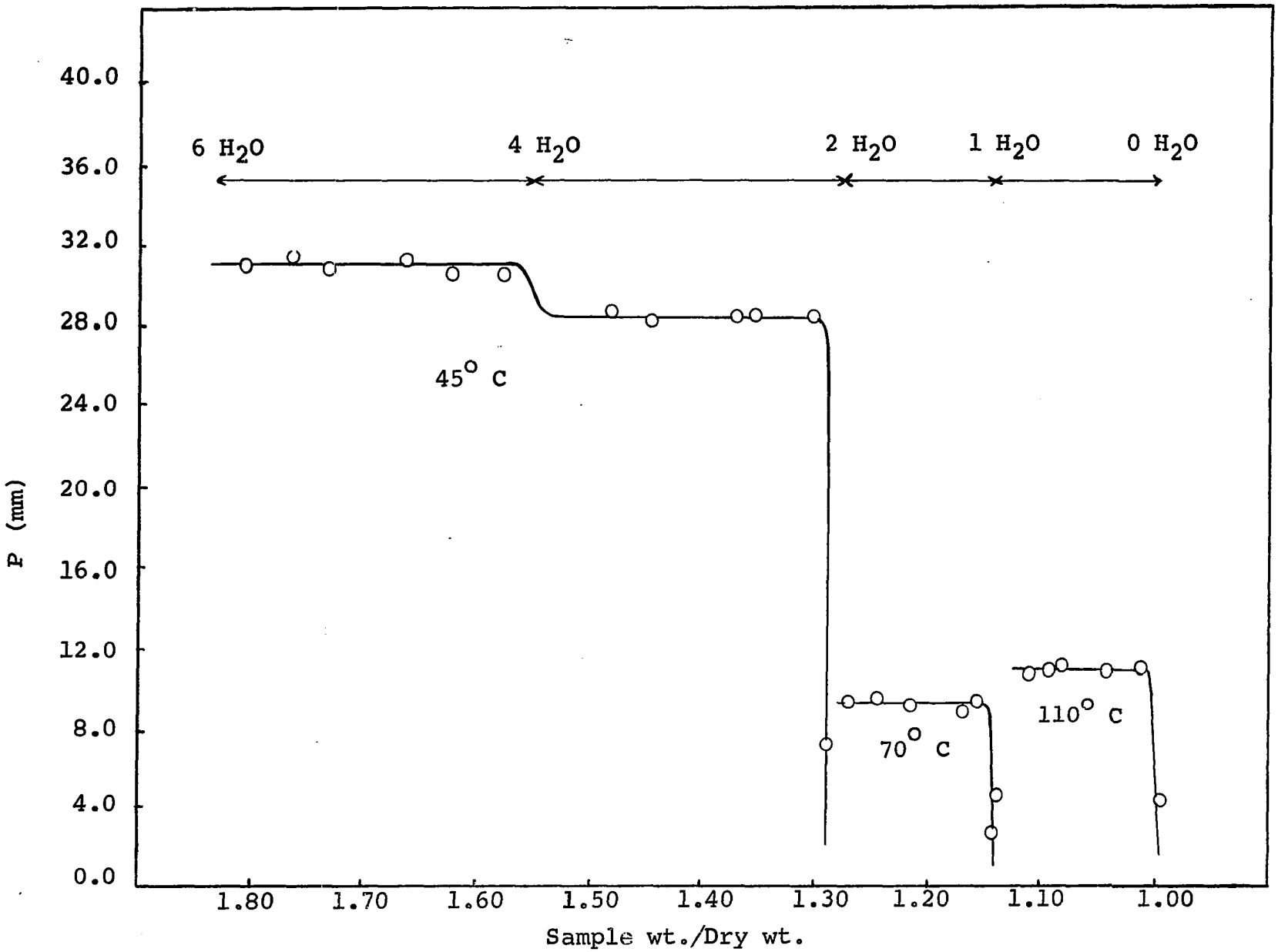


Figure 2. Dissociation Pressures of $CoCl_2$ Hydrates as a Function of Composition

Table 1

Dissociation Pressures for $CoCl_2$ Hydrates

as a Function of Composition

P (mm)	sample wt./dry wt.	moles H_2O
$CoCl_2.6H_2O$ at 45.0° C		
31.2	1.801	5.56
30.9	1.763	5.29
31.1	1.723	5.02
31.2	1.635	4.41
30.7	1.610	4.23
30.8	1.584	4.05
$CoCl_2.4H_2O$ at 45.0° C		
28.1	1.545	3.78
28.3	1.495	3.42
27.5	1.452	3.14
28.2	1.376	2.61
28.4	1.365	2.51
28.2	1.297	2.07
6.4	1.290	2.05

Table 1 (Cont.)

$CoCl_2.2H_2O$ at 70° C

P (mm)	sample wt./dry wt.	moles H_2O
10.2	1.286	1.98
10.1	1.282	1.96
10.0	1.261	1.82
10.1	1.242	1.68
9.8	1.189	1.31
10.1	1.163	1.13
4.8	1.152	1.05
1.9	1.151	1.04

$CoCl_2.H_2O$ at 110° C

12.1	1.124	0.86
11.8	1.107	0.74
12.4	1.097	0.67
12.2	1.054	0.37
11.7	1.011	0.06
3.2	1.002	0.01

$$CoCl_2.6H_2O_{(s)} = CoCl_2.4H_2O_{(s)} + 2\ H_2O_{(g)} \quad (1)$$

$$CoCl_2.4H_2O_{(s)} = CoCl_2.2H_2O_{(s)} + 2\ H_2O_{(g)} \quad (2)$$

$$CoCl_2.2H_2O_{(s)} = CoCl_2.H_2O_{(s)} + H_2O_{(g)} \quad (3)$$

$$CoCl_2.H_2O_{(s)} = CoCl_{2(s)} + H_2O_{(g)} \quad (4)$$

The dissociation pressures of the hydrates, $CoCl_2.6H_2O$, $CoCl_2.4H_2O$, and $CoCl_2.2H_2O$ were studied as a function of temperature. A new sample of hexahydrate was placed in the vacuum system, and the pressure was measured at a series of temperatures between 25° C and 50° C. There was no evidence for a pentahydrate in the pressure vs. composition work, and this was further checked by measuring the pressure for a sample whose composition corresponded to a pentahydrate. The pressure was identical to that observed for the hexahydrate.

The tetrahydrate pressure was measured over the same temperature range and was found to be lower than for the hexahydrate. The pressure of a sample corresponding in composition by weight to a trihydrate was measured and found to be the same as the tetrahydrate.

The procedure was repeated for $CoCl_2.2H_2O$ over the temperature range from 50° - 85° C and for $CoCl_2.H_2O$ over the range 85° - 110° C.

The results are shown in figures 3 and 4.

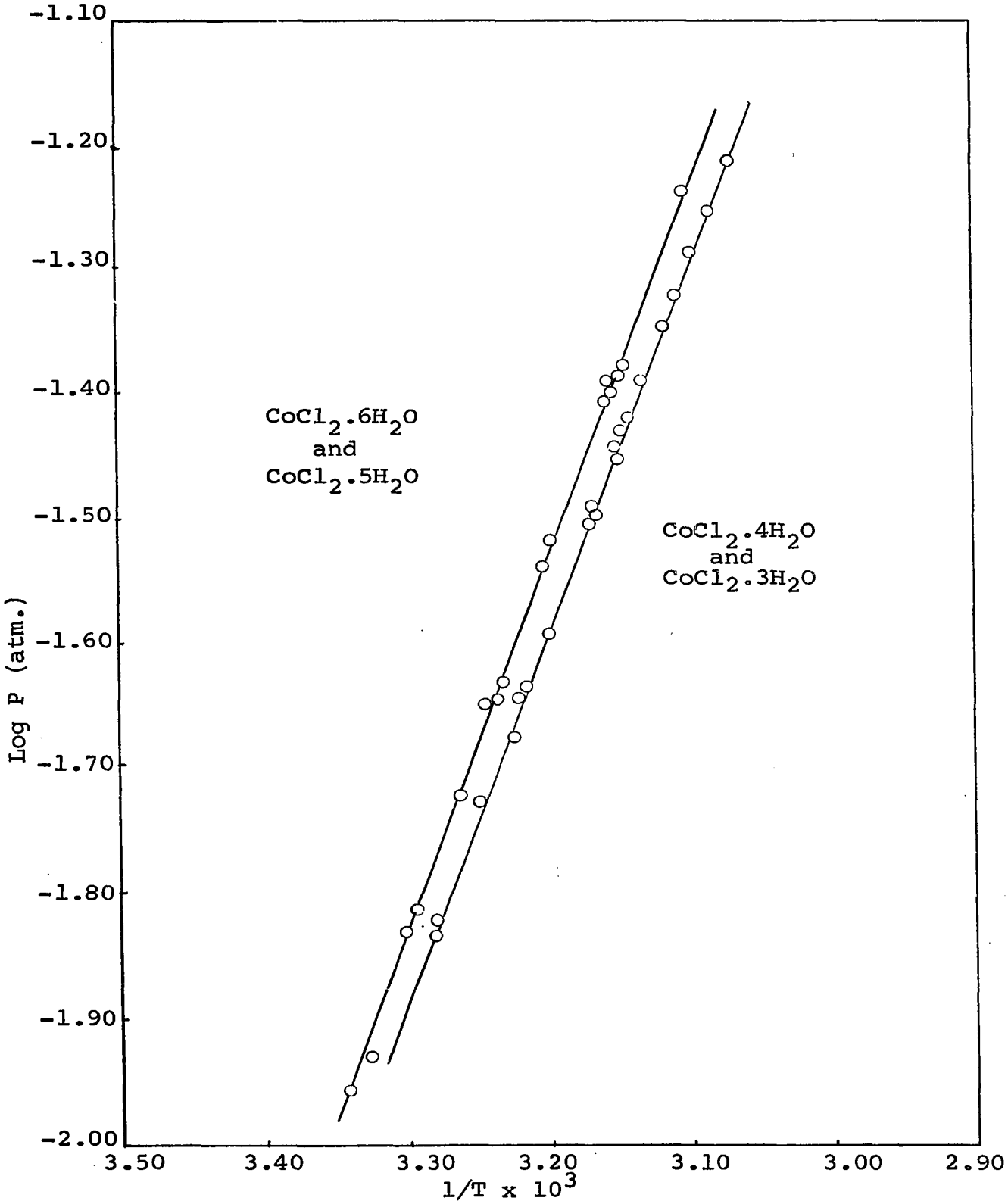


Figure 3. Dissociation Pressure of $CoCl_2.6H_2O$ and $CoCl_2.4H_2O$ as a Function of Temperature

Table 2

Dissociation Pressures of $CoCl_2.6H_2O$ and $CoCl_2.4H_2O$ as f (T)

$CoCl_2.6H_2O$			
T ^oK	$1/T \times 10^3$	P 0^oC (mm)	Log P (atm)
299.4	3.340	8.0	-1.978
302.7	3.304	10.6	-1.857
303.9	3.291	11.4	-1.824
307.0	3.257	14.1	-1.730
309.5	3.231	16.8	-1.656
313.0	3.195	21.4	-1.550
317.7	3.148	29.6	-1.410
318.5	3.140	31.3	-1.385
323.2	3.095	44.2	-1.235
$CoCl_2.4H_2O$			
299.0	3.344	7.4	-2.012
304.3	3.286	10.9	-1.845
304.5	3.284	10.7	-1.851
306.2	3.266	12.3	-1.790
307.6	3.251	13.6	-1.747
310.6	3.220	16.9	-1.654
312.2	3.203	18.9	-1.604
315.2	3.173	23.1	-1.517

Table 2 (Contd)

318.0	3.145	28.1	-1.432
322.0	3.106	36.3	-1.321
324.2	3.084	42.7	-1.250
329.0	3.040	55.6	-1.136

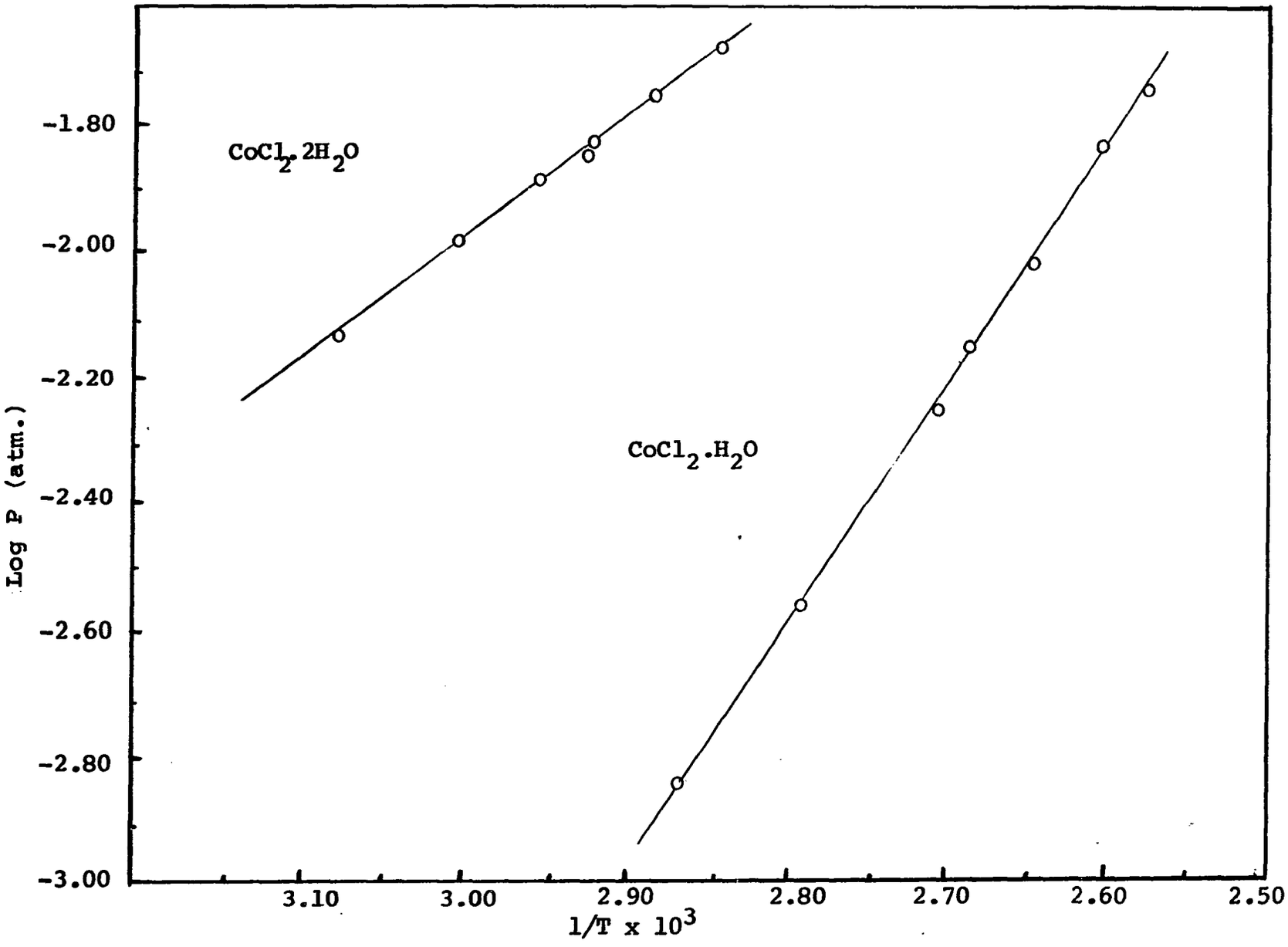


Figure 4. Dissociation Pressure of $CoCl_2.2H_2O$ and $CoCl_2.H_2O$ as a Function of Temperature

Table 3

Dissociation Pressures of $CoCl_2.2H_2O$ and $CoCl_2.H_2O$ as f(T)

$CoCl_2.2H_2O$

T ^oK	1/T x 10^3	P 0^oC(mm)	Log P (atm)
325.2	3.075	5.4	-2.149
333.2	3.001	7.9	-1.983
339.0	2.950	9.7	-1.894
342.0	2.924	10.5	-1.859
343.0	2.915	11.4	-1.824
348.3	2.871	14.1	-1.732
353.3	2.830	16.7	-1.658

$CoCl_2.H_2O$

348.4	2.870	1.1	-2.839
358.4	2.790	2.2	-2.539
368.0	2.717	4.1	-2.268
372.4	2.685	5.7	-2.125
378.1	2.645	7.5	-2.006
383.0	2.611	11.4	-1.824
387.6	2.580	13.9	-1.738

Table 4

Thermodynamic Constants at 30° for

the Dehydration Reactions

	ΔH^{o} cal/mole	ΔF^{o} cal/mole	ΔS^{o} e.u./mole
$CoCl_2.6H_2O = CoCl_2.4H_2O + 2H_2O$	26,810	5,130	71.5
$CoCl_2.4H_2O = CoCl_2.2H_2O + 2H_2O$	26,820	5,230	71.2
$CoCl_2.2H_2O = CoCl_2.H_2O + H_2O$	9,060	3,590	18.0
$CoCl_2.H_2O = CoCl_2 + H_2O$	18,040	6,320	38.7

Calculations

Since only the water is in the gaseous state and the pressure is low enough so it can be treated as ideal, the variation in dissociation pressure with temperature for each dissociation step was fitted to the equation,

$$\text{Log } P = - \Delta H^{\circ}/2.303\ nRT + \Delta S^{\circ}/2.303\ nR \quad (5),$$

where P is the pressure in atmospheres, T is the temperature in degrees absolute, ΔH° and ΔS° are respectively the standard enthalpy and entropy for the reactions, and n is the number of moles of water lost.

For each reaction, log P was plotted against 1/T with the slope equal to $- \Delta H^{\circ}/2.303\ nR$. The standard free energy, ΔF° for each reaction was calculated at 30° C from the equation:

$$\Delta F = -2.303\ nRT \log P \quad (6)$$

The standard entropy could be found from the intercept in equation 5 or from the relationship

$$\Delta S^{\circ} = \frac{\Delta H^{\circ} - \Delta F^{\circ}}{T} \quad (7)$$

The thermodynamic values are reported in table 4.

From the known enthalpy and entropy of formation of anhydrous cobalt chloride[6] and the values reported in table 4, the enthalpy and entropy of formation for the individual hydrates can be found. The results (at 30° C) are given in

table 5 along with the heats of formation (at 25° C) which have been reported by other investigators. The reported values are in very good agreement (within 2%) with the literature values for the heats of formation.

Discussion

The enthalpy change involved in removing the first four moles of water from the hexahydrate is 13.41 Kcal per mole of water. This is very close to the enthalpy change required to change one mole of ice to one mole of water vapor at 30° C (approximately 12.4 Kcal/mole). The enthalpy change for removing the next mole of water from the dihydrate is 9.06 Kcal, the lowest value for any step. The last mole of water, lost from the monohydrate, requires 18.04 Kcal.

For comparison, the enthalpy change per mole of water lost for $Co(en)_2Cl_2.Cl.6H_2O.HCl$ is 11 Kcal[7]. From a comparison of these values, only the last mole of water to be removed appears to have an unusual bond strength.

The entropy change required to change one mole of ice to water vapor at 30° C is 35.1 e.u.* If we compare the entropy change for taking one mole of water in the solid

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*Calculated from the data in N. A. Lange and G. M. Forker, Editors "Handbook of Chemistry", 9th Ed. Handbook Publishers, Inc., Sandusky, Ohio, 1956 pp. 1538 ff.

TABLE 5

Enthalpy and Entropy of Formation of the

Solid Cobalt(II) Chloride Hydrates at 30° C

Compound	ΔH formation Kcal/mole		ΔS formation e.u./mole	Change in S_f e.u./ mole
	Experimental	Literature[6]		
$CoCl_2$		-77.7	25.7	
				-6.5
$CoCl_2.H_2O$	-153.5		32.2	
				-27.1
$CoCl_2.2H_2O$	-220.4	-222.9	59.3	
				-19.2
$CoCl_2.4H_2O$	-362.8	-367.2	78.5	
				-18.9
$CoCl_2.6H_2O$	-505.2	-508.9	97.4	

hydrate to the vapor phase with the value for ice, an observed value lower than 35.1 e.u./mole will indicate ordering in the solid phase, and a value above 35.1 e.u./mole will indicate disordering in the solid phase.

The data in table 4 indicate almost no change in the solid phase with the loss of the first four moles of water from the hexahydrate. The loss of the last mole of water from the monohydrate produces only a small change, and it is only the loss of one mole of water from the dihydrate that produces an appreciable change in the crystalline structure.

The differences between the entropies of formation of the hydrates also indicate the small difference between the anhydrous and monohydrate compounds and the much larger difference between the monohydrate and dihydrate. The changes between the dihydrate, tetrahydrate, and hexahydrate are intermediate between the other values.

CHAPTER IV

SPECTRA

Experimental

Samples of $CoCl_2.6H_2O$, $CoCl_2.4H_2O$, $CoCl_2.2H_2O$, $CoCl_2$, and samples with composition by weight corresponding to $CoCl_2.5H_2O$ and $CoCl_2.3H_2O$ were prepared by methods described in chapter II.

Glass slides with a recessed area were filled with the powdered samples, and a thin cover glass was sealed over the sample to eliminate changes in hydration. A reference sample of magnesium oxide was prepared in the same manner. The cover plates were shown to be invisible to light in the spectral region used by measuring the spectra of MgO samples both covered and uncovered. No difference was observed between the two cases.

All spectra were measured on a Beckman Model DK-1 double beam ratio recording spectrophotometer equipped with a reflectance attachment. The radiation source for the near infrared and visible regions of the spectrum was a six volt

incadescent tungsten lamp. The prism was cut from a single silica crystal and had a high dispersion in the near infrared region. A lead sulfide cell served as detector above 700 millimicrons and a photomultiplier tube below 700. The instrument was equipped with a modified Brown potentiometric strip recorder which recorded linearly in percent transmittance or absorbancy. The diffusion sphere was recoated twice with freshly ignited magnesium oxide during the measurements.

The spectrum of each compound was measured with at least two different samples. The agreement between measurements was excellent.

The spectra are given in figures 5 - 9. Molar absorbancy indices were not calculated, and peak heights are shown relative to one another.

Calculations

The spectra of $CoCl_2.6H_2O$, $CoCl_2.4H_2O$, $CoCl_2.2H_2O$, and $CoCl_2.H_2O$ are all very similar in overall appearance but have small and very important differences. The series of peaks in the low energy part of the spectra are almost identical but shift slightly to lower energies with the lower hydrates. The major band in the visible region shows the greatest change, also shifting to lower energy with fewer

waters of hydration. This would be expected since the color changes from red to blue as waters are removed from the hexahydrate.

The energy level diagram for the energy states of a cobalt(II) compound is shown in figure 10. The tetragonal distortion part of this diagram was calculated by Dr. Norman Fogel, University of Oklahoma, on the basis of weak field with a ^4F ground state and ^4P as the principal excited state. The distorted energy levels are in error by approximately 1-2% for the calculated values of Dq, Ds, and Dt, but a more exact expression did not seem necessary. The diagram as given is good for any octahedrally coordinated d^7 compound with regular cubic or tetragonally distorted symmetry. For the energy levels of tetrahedrally coordinated d^7 compounds the diagram should be inverted.

Anhydrous $CoCl_2$ and all of its hydrates are assigned the cubic field octahedral configuration. As can be seen from the energy level diagram, a regular or symmetric cubic field splits the ^4F ground state into three energy levels, $^4T_{1g}$, $^4T_{2g}$, and $^4A_{2g}$. Another $^4T_{1g}$ level also arises from the ^4P excited state. With the $^4T_{1g}$ (F) (i.e. $^4T_{1g}$ from the F state) as the ground state, three d-d transitions should be observed in the spectrum if a symmetric cubic field existed.

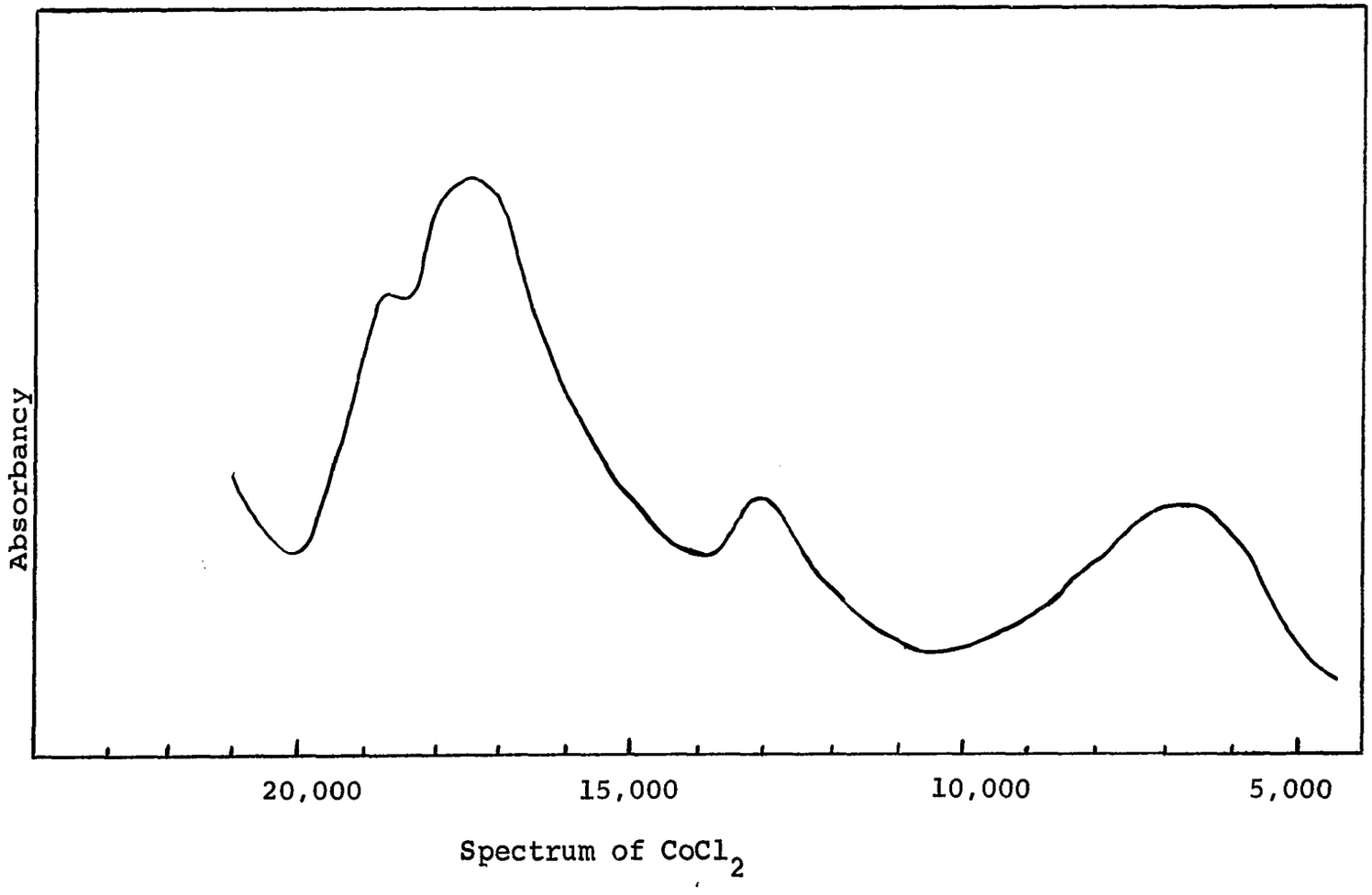


Figure 5

Figure 6

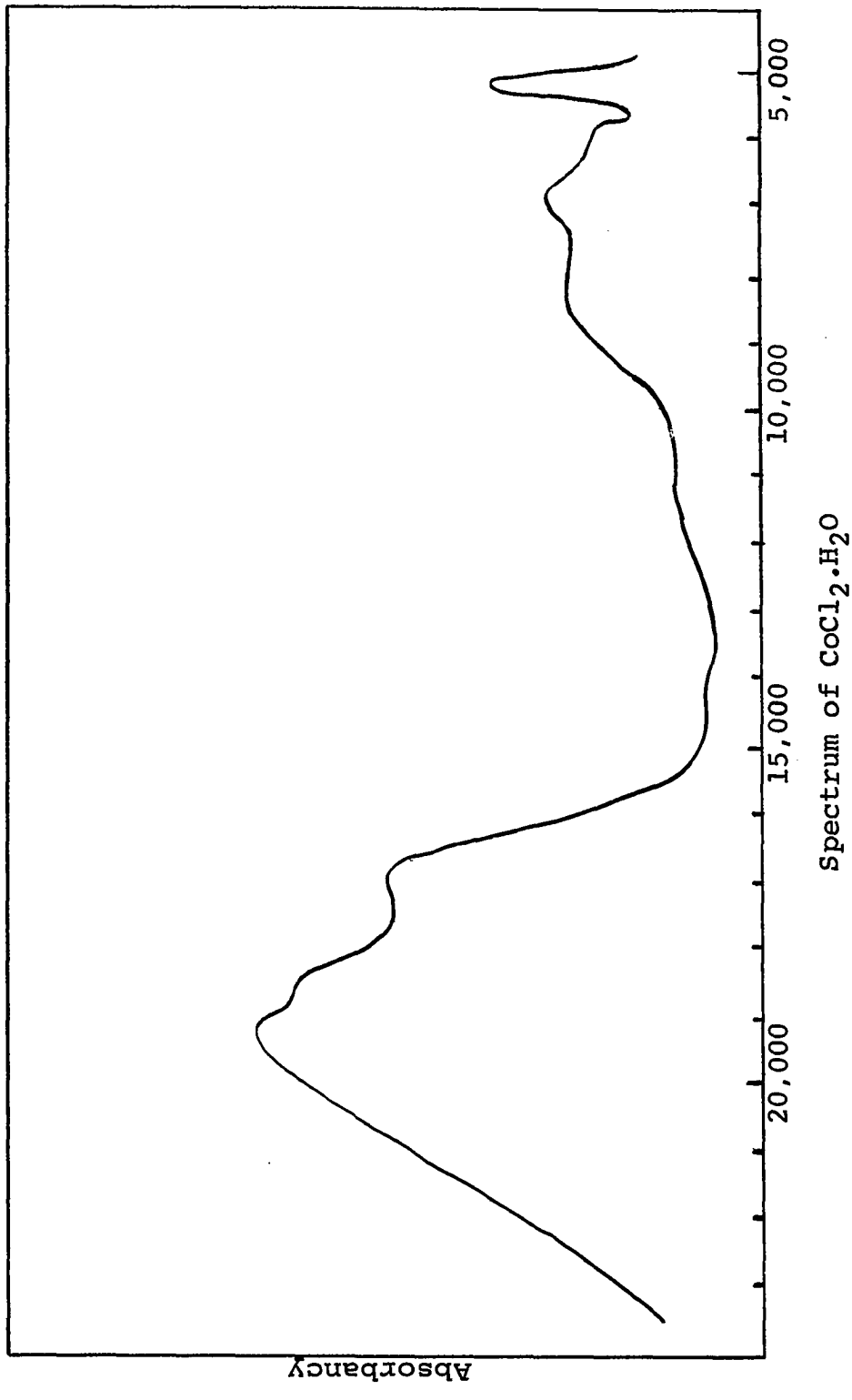


Figure 7

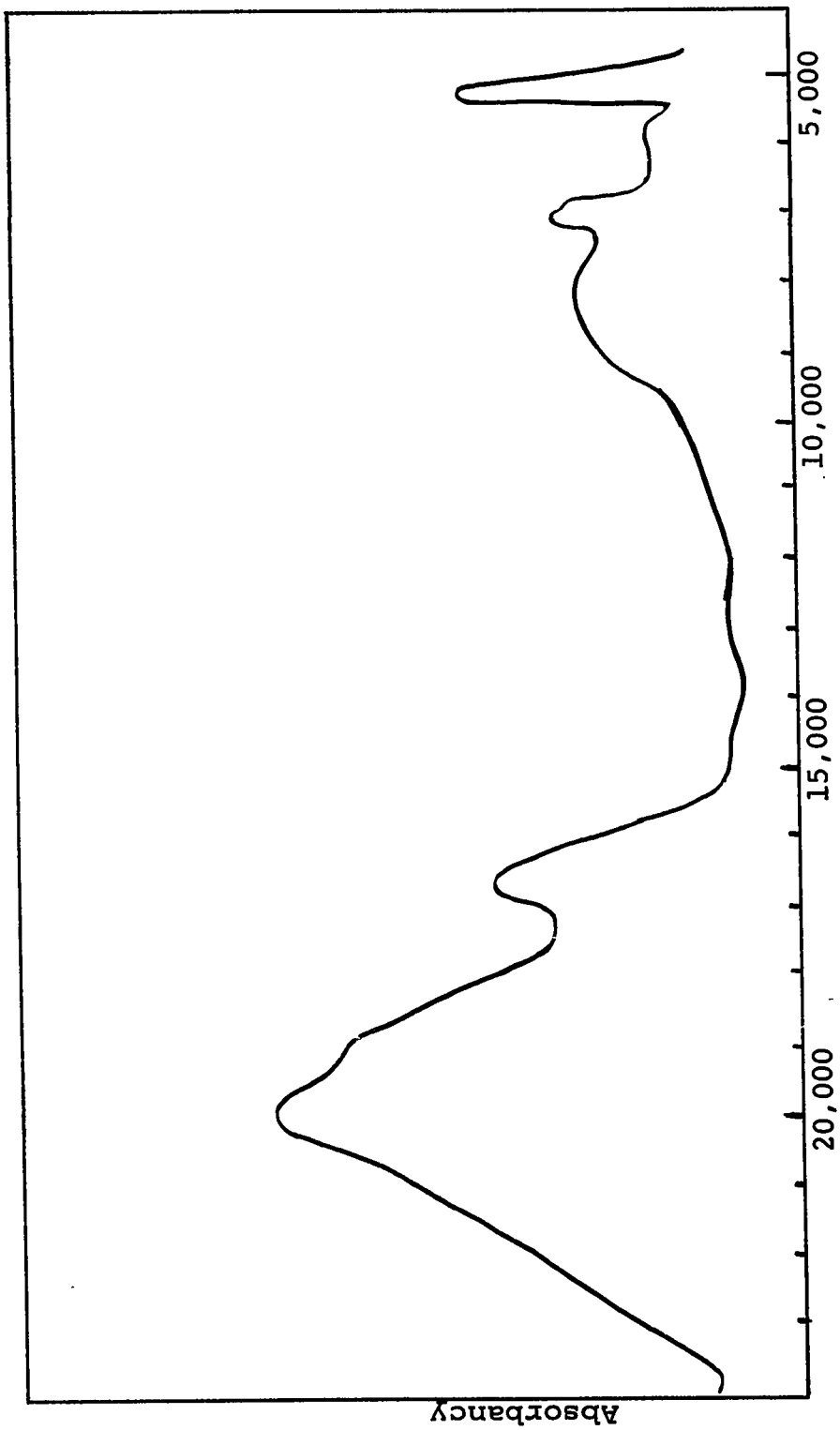

Absorbancy
5,000
10,000
15,000
20,000
Spectrum of $CoCl_2 \cdot 2H_2O$

Figure 8

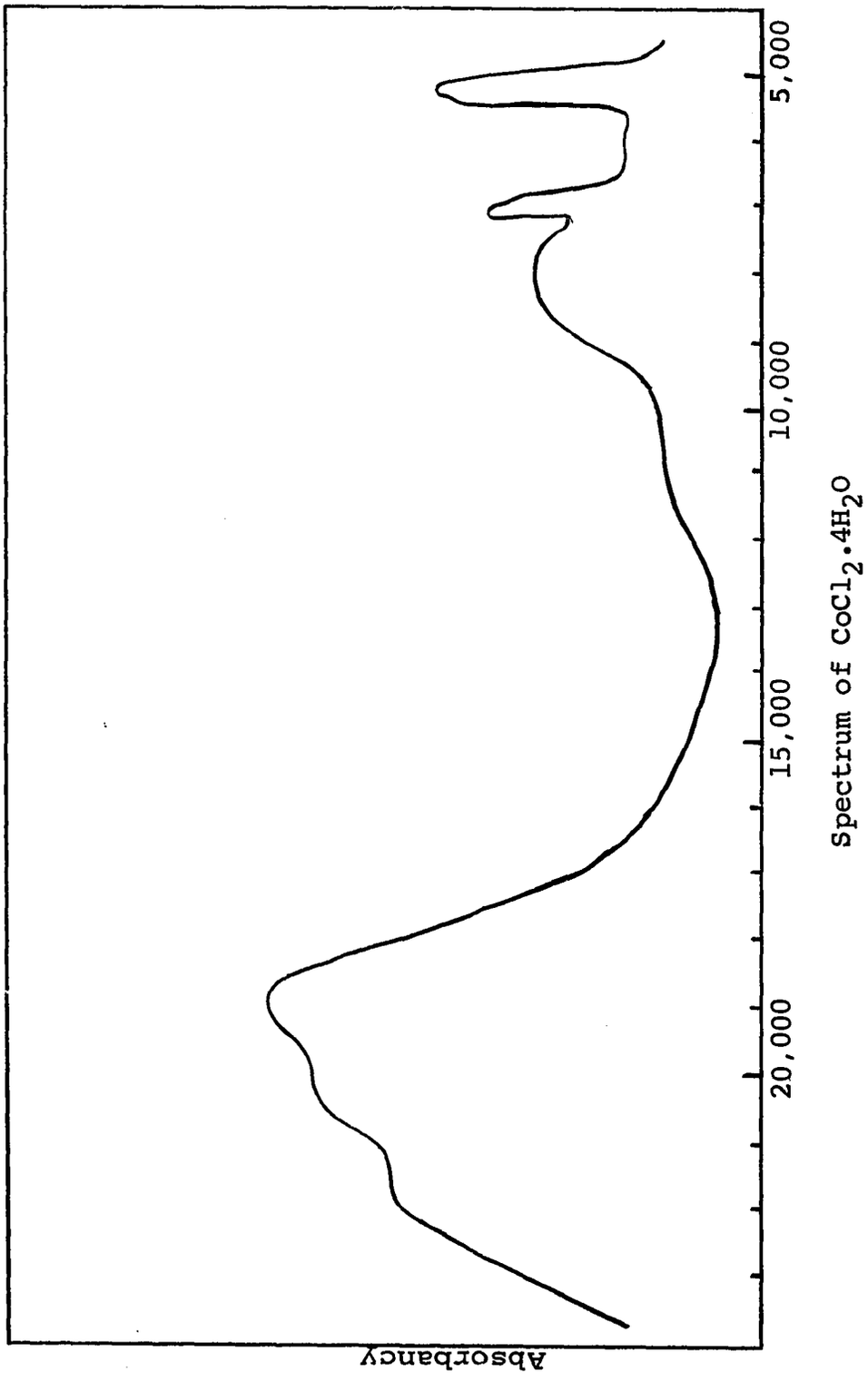
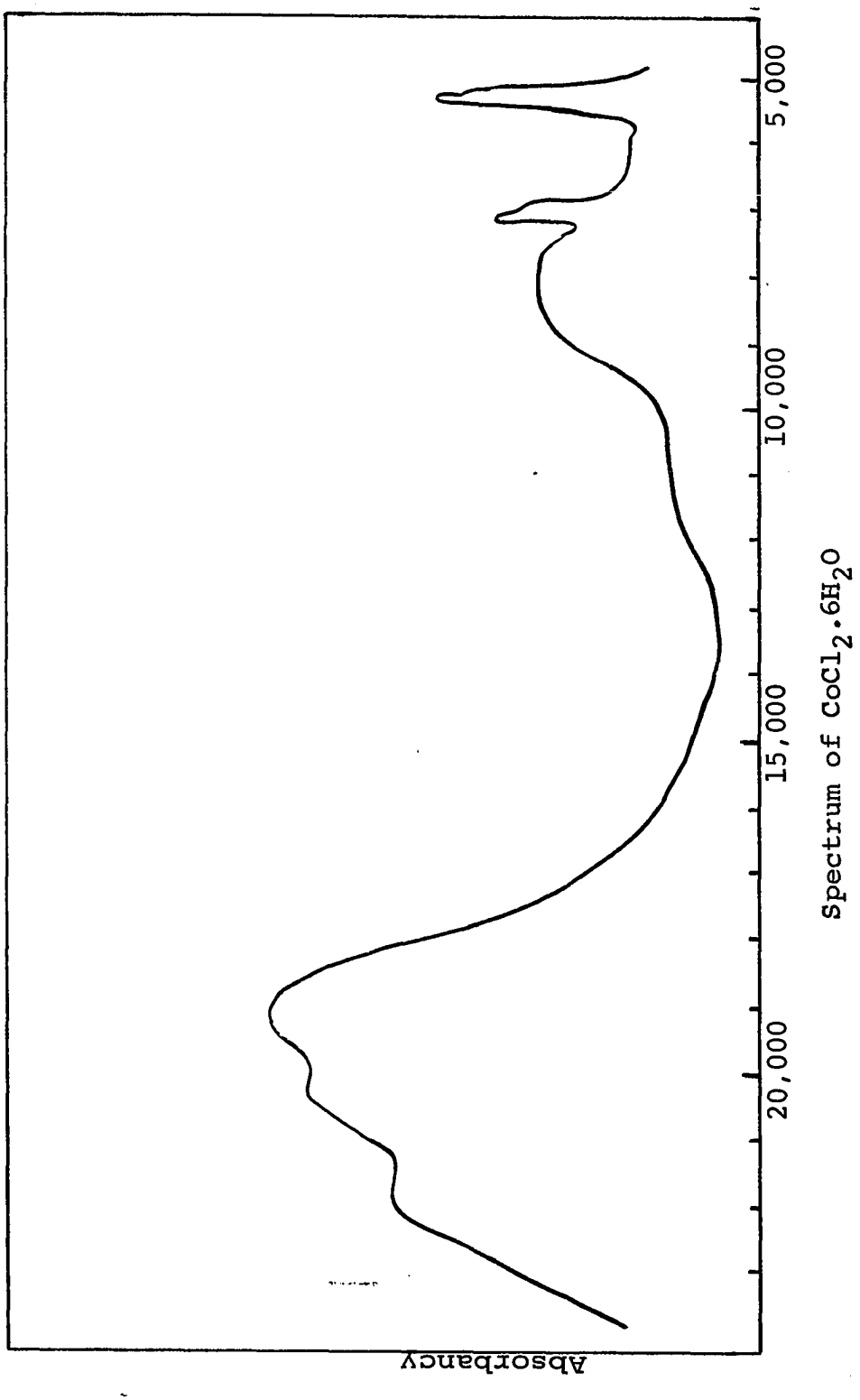

Absorbancy
5,000
10,000
15,000
20,000
Spectrum of $CoCl_2 \cdot 4H_2O$

Figure 9


Absorbancy
5,000
10,000
15,000
20,000
Spectrum of $CoCl_2 \cdot 6H_2O$

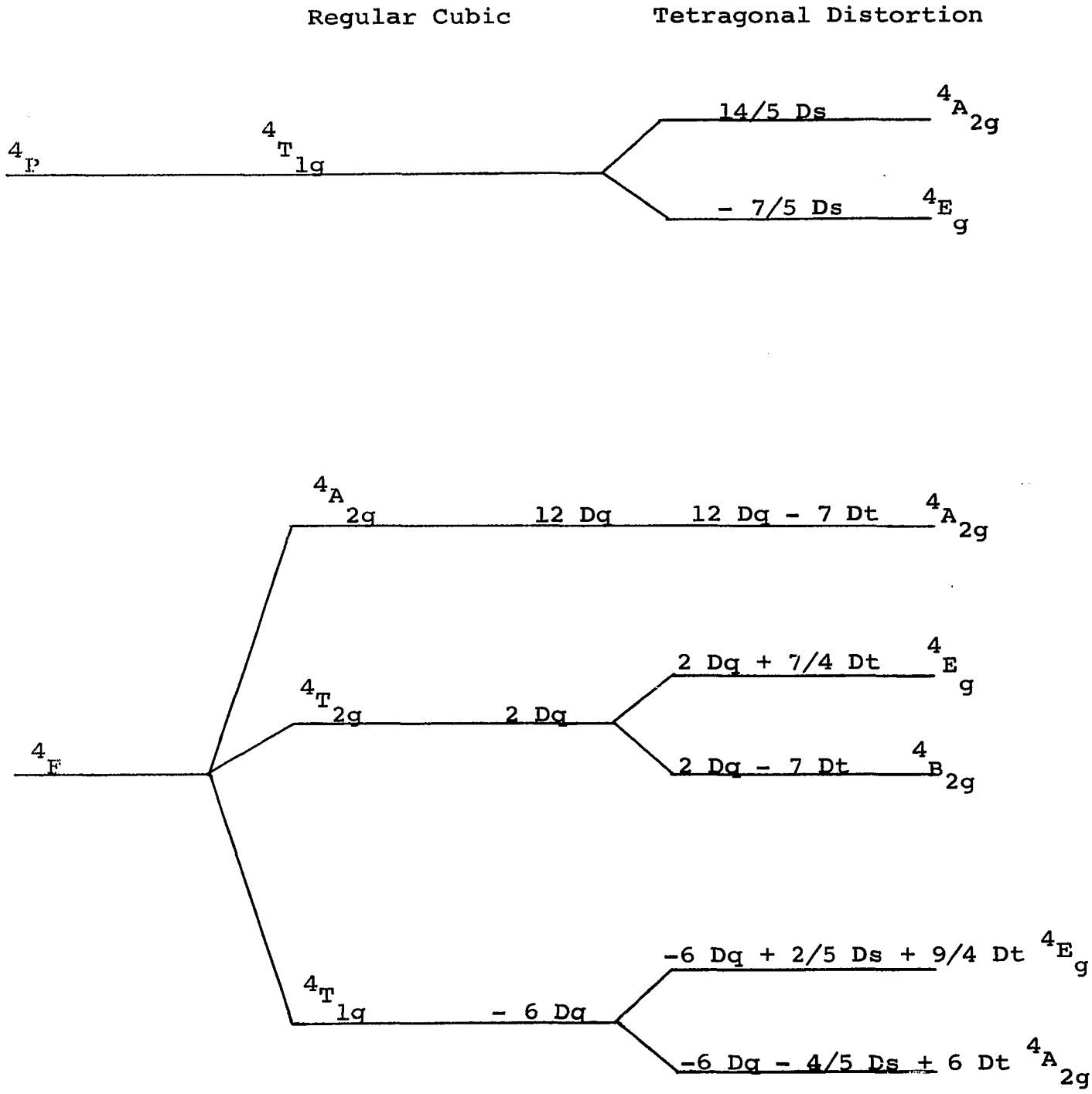


Fig. 10. Energy Level Diagram for Octahedral d^7. Invert for Tetrahedral d^7.

The energies at which the transitions occur in a weak field case correspond to:

$$\nu_1 = 8\ Dq \qquad {}^4T_{1g}\ (F) \rightarrow {}^4T_{2g} \qquad (8)$$

$$\nu_2 = 18\ Dq \qquad {}^4T_{1g}\ (F) \rightarrow {}^4A_{2g} \qquad (9)$$

$$\nu_3 = 6\ Dq + ({}^4P - {}^4F) \qquad {}^4T_{1g}\ (F) \rightarrow {}^4T_{1g}\ (P) \qquad (10)$$

where 10 Dq = Δ, (the cubic field splitting parameter), and ${}^4P - {}^4F$ is the energy difference between the ${}^4F$ and ${}^4P$ states (approximately 14,500 cm^{-1} for Co^{+2}).

Only anhydrous $CoCl_2$ has a spectrum fitting these conditions. It is, therefore, considered to have a fairly symmetrical, octahedrally coordinated crystal lattice. The splitting of the major band at approximately 17,850 cm^{-1} has been explained by other investigators as being due to spin-orbit coupling.

All of the hydrates show more bands than can be explained by a symmetrical structure, especially in the region where the first transition would be expected (around 6500 cm^{-1}). The most probable reason for this splitting is tetragonal distortion (two groups are either at a smaller or larger distance from the central metal ion than the other four groups). Tetragonal distortion further splits the ${}^4T_{1g}(F)$, ${}^4T_{2g}$, and ${}^4T_{1g}(P)$ energy states as shown on the right in figure 10. The first and third transitions would

be broken into four peaks each and the second transition into two peaks. If the assumption of tetragonal distortion is true, a better fit of the spectra should be obtained by using the distortion splitting parameters Ds and Dt. (Ds is the second power splitting parameter and Dt is the fourth power splitting parameter.)

An approximate value for Dq was obtained from the center of each complex band, and various values of Ds and Dt were tried until the best fit was obtained. The best values for Dq, Ds, and Dt for each compound are given in table 6.

TABLE 6

	Dq	Ds	Dt
$CoCl_2.6H_2O$	900	360	180
$CoCl_2.4H_2O$	900	360	180
$CoCl_2.2H_2O$	850	-220	110
$CoCl_2.H_2O$	840	-200	100
$CoCl_2$	750		

Values of Dq, Ds, and Dt are in cm^{-1}.

The positions of the observed bands and the calculated values are given in tables 7 - 11 with all values reported in cm^{-1}.

Since the coordination spheres of the hydrates are composed of water molecules and chloride ions, an average field

TABLE 7

Spectrum of $CoCl_2$

Observed Center of Band	Description	Calculated
6,450	Broad, fairly symmetrical	6,000
7,630	Shoulder on first band	
13,510	Weak	13,520
17,550	Broad, intense	18,500
18,870	Shoulder	

All values reported in cm^{-1}

$Dq = 750\ cm^{-1}$

TABLE 8

Spectrum of $CoCl_2 \cdot H_2O$

Observed Center of Band		Description	Calculated
1.	5,220	Sharp, medium low intensity	5,260
2.	5,870	Broad band composed of several peaks difficult to separate	5,875
	6,250		6,135
	6,970		6,750
3.	7,930	Low, broad peak	13,660
4.	14,080	Low intensity peak	14,275
5.	17,100	Complex band, Possible to separate into four peaks	18,220
	18,870		18,675
	19,420		18,835
	24,400		19,060

All values reported in cm^{-1}

$Dq = 840\ cm^{-1}$

$Ds = -200\ cm^{-1}$

$Dt = 100\ cm^{-1}$

TABLE 9

Spectrum of $CoCl_2.2H_2O$

	Observed Center of Band	Description	Calculated
1.	5,210	Sharp, fairly intense peak	5,194
2.	5,720	Weak, unsymmetrical peak	5,625
	5,850	Composed of two peaks	5,870
3.	6,890	Fairly broad band, composed of two peaks	6,833
	7,140		
4.	7,940	Low, broad peak	
5.	13,000	Low intensity peaks	13,694
	14,490		14,370
6.	16,950	Broad, complex band, possible to separate into five individual peaks	18,184
	19,220		18,824
	19,610		19,072
	20,000		19,748
	23,850		

$Dq = 850\ cm^{-1}$

$Ds = -220\ cm^{-1}$

$Dt = 110\ cm^{-1}$

TABLE 10

Spectrum of $CoCl_2 \cdot 4H_2O$

Observed Center of Band		Description	Calculated
1.	5,130	Sharp band composed of two single peaks	5,148
	5,280		5,391
2.	6,890	Sharp band composed of two separate peaks	6,723
	7,140		6,966
3.	8,270	Low broad peak	
4.	14,810	Low intensity peak	14,148
			14,391
5.	16,520		
	18,550	Broad complex band; Possible to separate into five individual peaks	18,604
	18,880		18,847
	20,210		20,116
	21,750		20,359

All values reported in cm^{-1}

$Dq = 900\ cm^{-1}$

$Ds = 360\ cm^{-1}$

$Dt = 180\ cm^{-1}$

TABLE 11

Spectrum of $CoCl_2.6H_2O$

Observed Center of Band		Description	Calculated
1.	5,130	Sharp band composed of two single peaks	5,148
	5,270		5,391
2.	6,900	Sharp band composed of two single peaks	6,723
	7,140		6,966
3.	8,330	Low broad peak	14,148
4.	14,920	Low intensity peak	14,391
5.	18,880	Broad, complex band possible to separate into four individual peaks	18,604
	19,420		18,847
	20,410		20,116
	21,990		20,359

All values in cm^{-1}

$Dq = 900\ cm^{-1}$

$Ds = 360\ cm^{-1}$

$Dt = 180\ cm^{-1}$

approximation will indicate the expected values for Dq.

$$Dq_{hydrate} = n/6\ Dq_{H_2O} + m/6\ Dq_{Cl^-}$$

where n is the number of moles of water and m is the number of moles of chloride ion in the coordination sphere.

If Dq_{H_2O} is taken from the solution spectrum of $Co(H_2O)_6^{+2}$ as 950 cm^{-1} and Dq_{Cl^-} is taken from the spectrum of anhydrous $CoCl_2$ as 750 cm^{-1}, the values obtained are given in table 12.

TABLE 12

Average Field Approximation for $CoCl_2$ Hydrates

	Coordination Sphere		$Dq_{(calc.)}$	$Dq_{(obs.)}$
$CoCl_2.6H_2O$	6 H_2O	0 Cl^-	950	900
	or 4 H_2O	2 Cl^-	880	900
$CoCl_2.4H_2O$	4 H_2O	2 Cl^-	880	900
$CoCl_2.2H_2O$	2 H_2O	4 Cl^-	820	850
$CoCl_2.H_2O$	2 H_2O	4 Cl^-	820	840
	or 1 H_2O	5 Cl^-	780	840

All values of Dq in cm^{-1}

Discussion

The spectrum of $CoCl_2$ is composed of three fairly symmetrical bands. This is in agreement with what is expected for a non-distorted octahedral compound with three possible transitions as indicated in figure 10. The peak in the near

infrared region of the spectrum appears to be made up of several bands which may indicate slight distortion. However, the resolution is too low to attempt fitting any type of distortion. The splitting of the visible band has been attributed by Koide to spin-orbit splitting of the $^4T_{1g}(P)$ energy level[8]. This may account for the extra band in the spectrum of $CoCl_2$ and also for the highest energy peak which appears in the spectra of the hydrates.

The spectra of $CoCl_2.6H_2O$ and $CoCl_2.4H_2O$ are badly fragmented and almost identical. X-ray analysis of the hexahydrate indicates the correct formula is $Co(H_2O)_4Cl_2.2H_2O$, with the water molecules closer to the cobalt ion than the chloride ions (tetragonal distortion). If the first two molecules of water lost from the hexahydrate are the non-coordinated water molecules in water-like positions outside of the inner coordination sphere, then the inner coordination sphere of the hexahydrate and tetrahydrate would be the same. This would explain the almost identical spectra observed for the two compounds.

The observed spectra for the hexahydrate and tetrahydrate were fitted to the distortion equations with the same values for Dq, Ds, and Dt giving reasonably good agreement in each case. The positive values for Ds are in agreement

with axial elongation of the tetragonal structures as indicated by the x-ray structure of the hexahydrate which found the two chloride ions at a greater distance from the cobalt ion than the water molecules. The agreement between the calculated and observed values for the spectra indicate that the major distortion is tetragonal although other minor types of distortion are probably present as indicated by the spectra and the x-ray analysis of the hexahydrate.

The spectra of the dihydrate and monohydrate are almost identical but slightly different from the hexa- and tetrahydrate spectra. The positions of the peaks of the monohydrate agreed very closely with those of the dihydrate, but the bands in the low energy portion of the spectrum had a more symmetrical appearance. It appears to be an intermediate structure between the dihydrate and the anhydrous compound in agreement with the thermodynamic values. The monohydrate spectrum was fitted best with slightly lower values for Dq, Ds, and Dt indicating that the effect of the water was slightly reduced and that its structure was more symmetrical than the structure of the dihydrate. The negative values for Ds indicate axial compression with the water molecules closer to the cobalt ion than to the chloride ions. The most probable structure for the monohydrate, as indicated

by the spectrum, is two waters and four chloride ions around each cobalt ion probably in a polymeric, chain-like structure where water molecules link adjacent cobalt ions.

The spectra of samples prepared with compositions corresponding to $CoCl_2.3H_2O$ and $CoCl_2.5H_2O$ were taken. The spectrum of the pentahydrate corresponded to an average of the tetra and hexahydrate spectra, and the trihydrate spectrum corresponded to an average of the di- and tetrahydrate spectra. This helps confirm the indication from the dissociation pressures that neither a trihydrate nor pentahydrate forms under the conditions in this study.

CHAPTER V

MAGNETIC SUSCEPTIBILITY

Experimental

The magnetic susceptibilities of the compounds $CoCl_2.6H_2O$, $CoCl_2.4H_2O$, $CoCl_2.2H_2O$, $CoCl_2.H_2O$ and $CoCl_2$ were measured over the temperature range 77° K to approximately 300° K with a Curie-Chevenaux type balance (figure 11). The samples were prepared by methods discussed in chapter II.

Small samples of powdered compound (A) (.025 - .040 g) were suspended in a pyrex glass bucket with a silica fiber (B) from a torsion silica balance (C). (The force constant for the balance was found to be 1.7 mg/mm of travel by adding small calibrated aluminum weight to the empty bucket and measuring the distance of travel.) The entire assembly was enclosed in a glass system (D) which could be evacuated through a stopcock (E). A specially prepared, silvered, Dewar flask (F) (evacuated to 10^{-7} mm Hg) was placed around the sample area and could be filled with various coolants (liquid nitrogen, dry-ice-acetone mixture, ice-alcohol

mixture or ice-water mixture). A calibrated double copper-constanan thermocouple (G) was placed near the sample and the temperature was measured by means of a Leeds and Northrup potentiometer. The sample chamber and Dewar fitted between the poles of a permanent magnet (H) which could be moved up or down by means of a screw drive and electric motor. A very fine silica fiber (I) was attached to the supporting fiber, and movement of the sample and fiber was measured with a Gaertner cathetometer (J) which could be read directly to .001 mm and was reproducible to ± .003 mm.

The magnetic balance was calibrated with pure Gd_2O_3 (99.999%) and small platinum rods. The gadolinium oxide was used as the primary standard since the paramagnetic susceptibility of platinum is very small. The calibration constant, k, for the balance was found to be 1.161×10^{-6} using Gd_2O_3 samples (.01 - .03 grams). The average value with Pt was 1.230×10^{-6}, but the deflection with platinum was so small ($0.120 \pm .005$ mm.) that the per cent error was too large for its use to be of value.

The pyrex glass sample bucket was found to be diamagnetic; so the amount of repulsion to the magnetic field was measured and used as a correction factor in equation 11. The value was 0.247 mm.

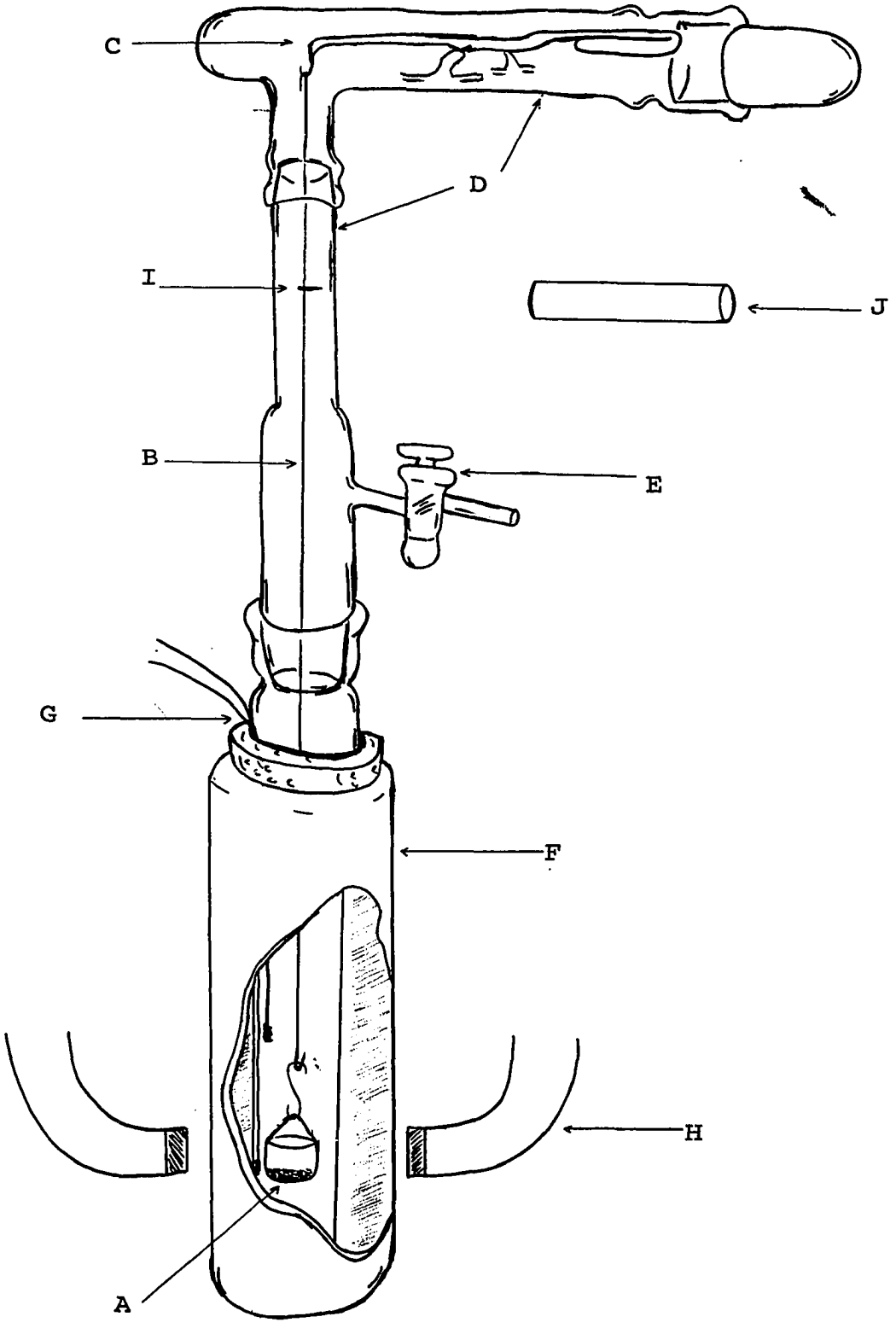


Diagram of Magnetic Balance

Each weighed sample was placed in the apparatus, and the system was evacuated. For lower temperature measurements, a small amount of air was readmitted through a calcium chloride drying tube to help establish faster temperature equilibrium between the sample and the coolant. With higher hydrates, the sample was cooled while the system was evacuated to prevent dehydration of the sample. After temperature equilibrium was reached, the magnet was swept past the sample, both up and down, and the movement of the sample was measured with the cathetometer until the maximum deflection was reached and the sample broke away from the magnetic field. The deflections up and down were added and, with the mass of the sample, used to calculate the gram susceptibility of the sample through equation 11.

Calculations

The deflection of the sample up and down and the mass of the sample gave the gram susceptibility, χ_g, at a particular temperature directly from the equation

$$\chi_g = \frac{k\ (d + d_{dia})}{M} \qquad (11)$$

where k is the calibration constant for the balance, d is the total deflection in millimeters, d_{dia} is the diamagnetism of the bucket, and M is the mass of the sample in grams. The

molar susceptibility was found from the equation

$$\chi_M = \chi_g \cdot F.W. \qquad (12)$$

where F.W. is the formula weight of the compound.

The compounds were found to follow the Curie-Weiss law

$$\chi_M = \frac{C_M}{T + \theta} \qquad (13)$$

where C_M is the Curie constant and θ is the Weiss constant. The equation can be rearranged to give

$$T = \frac{C_M}{\chi_M} - \theta \qquad (14)$$

A plot of T vs $1/\chi_M$ gives C_M as the slope and θ as the intercept on the T axis.

A more refined statement of the Curie Weiss law is

$$\chi_M = \frac{C_M}{T + \theta} + TIP \qquad (15)$$

where TIP is the temperature independent paramagnetism. A plot of χ_M vs $\frac{1}{T + \theta}$ will give a straight line with TIP the intercept on the χ_M axis. The Weiss constant can also be found by plotting χ_M vs $\frac{1}{T + \theta}$ with varying values of θ until the best straight line is obtained.

The effective magnetic moment, μ_{eff}, can be found from the Curie constant, or slope, in equation 15, from the relationship

$$C_M = \frac{1}{8} \cdot \mu^2_{eff} \qquad (16)$$

In figures 12 and 13, these plots are shown for $CoCl_2 \cdot 6H_2O$ to illustrate the method.

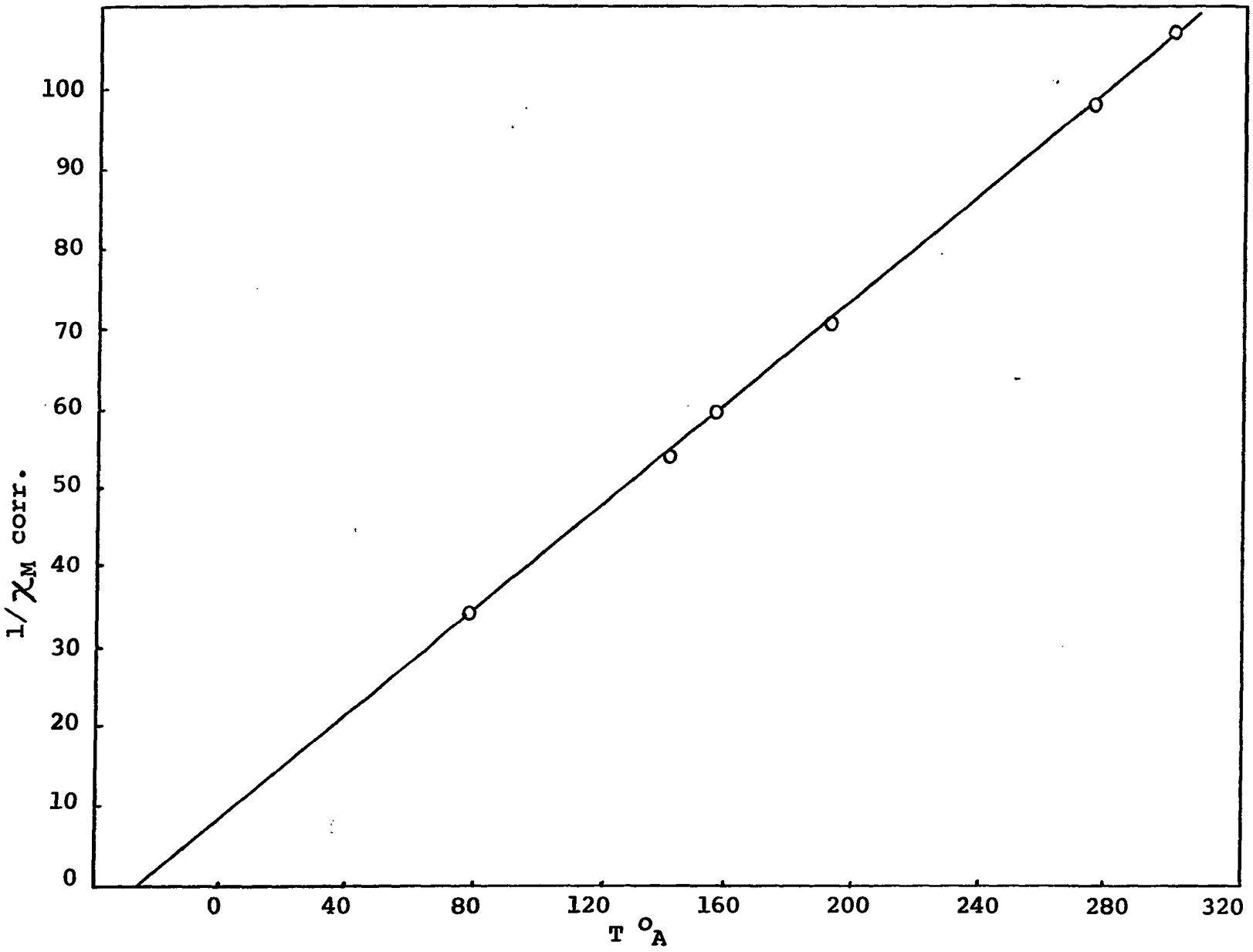


Figure 12 Plot of $1/\chi_M$ vs T for $CoCl_2.6H_2O$

TABLE 13

Plot of $1/\chi_M$ vs T for $CoCl_2.6H_2O$

$1/\chi_M$ (corrected)	T ^oK
104.1	300
95.4	274
68.1	189
58.1	156
52.5	139
33.0	77

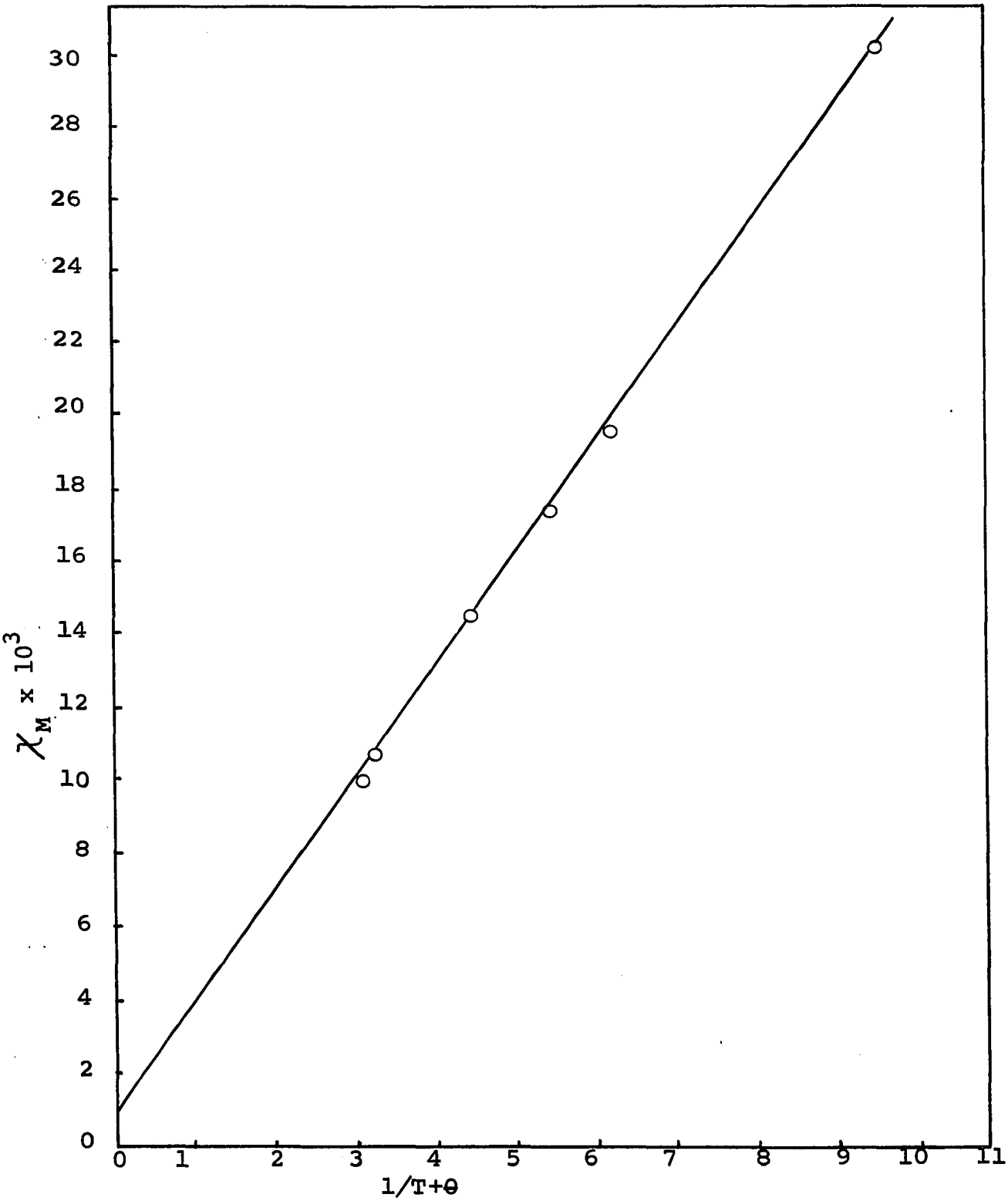


Figure 13 Plot of χ_M vs 1/T+θ for $CoCl_2.6H_2O$

TABLE 14

Plot of χ_M vs $\frac{1}{T + \theta}$ for $CoCl_2.6H_2O$

χ_M (corrected)	$\frac{1}{T + \theta}$
30.03	9.52
19.04	6.16
17.25	5.44
14.88	4.55
10.91	3.31
9.62	3.05

TABLE 15

Observed Magnetic Susceptibilities (in units of 10^{-3} C. G. S.-E. M. U. per mole) of $CoCl_2$

T ^{o}K	X_m (corrected)
301	13.02
275	14.60
265	15.40
200	20.52
77	63.47

μeff = 5.44 B. M. $\quad \theta = -19^{o}$ K. $\quad$ TIP = 0

Correction for diamagnetism = 0.06 x 10^{-3} c.g.s. unit

Lit. Value [10] $\quad \mu$eff = 5.37 B.M. $\quad \theta = -11^{o}$ K

TABLE 16

Observed Magnetic Susceptibilities (in units of 10^{-3} C. G. S.-E. M. U. per mole) of $CoCl_2.H_2O$

T °K	χ_M (corrected)
300	10.77
273	12.08
195	16.92
139	23.14
77	41.49

μeff = 5.16 B. M. θ = 3 °K TIP = 0

Correction for diamagnetism = 0.06 x 10^{-3} c.g.s. unit

TABLE 17

Observed Magnetic Susceptibilities (in units of 10^{-3} C. G. S.-E. M. U. per mole) of $CoCl_2.2H_2O$

T °K	χ_M (corrected)
291	10.88
280	11.33
235	13.19
192	16.81
77	38.45

μeff = 5.07 B.M. $\quad \theta = 7^{\circ}$ K $\quad$ TIP = 200 x 10^{-6} c.g.s. unit

Correction for diamagnetism = 0.06 x 10^{-3} c.g.s. unit

TABLE 18

Observed Magnetic Susceptibilities (in units of 10^{-3} C. G. S.-E. M. U. per mole) of $CoCl_2.4H_2O$

T ^{o}K	χ_M (corrected)
296	10.58
274	11.55
192	16.15
142	23.11
77	36.66

μ_{eff} = 5.13 B. M. $\quad \theta = 11^{o}$ K $\quad$ TIP = 0

Correction for diamagnetism = 0.06 x 10^{-3} c.g.s. unit.

TABLE 19

Observed Magnetic Susceptibilities (in units of 10^{-3} C. G. S.-E. M. U. per mole) of $CoCl_2.6H_2O$

T °K	χ_M (corrected)
300	9.62
274	10.91
192	14.88
156	17.25
138	19.04
77	30.03

μ_{eff} = 4.98 B. M. θ = 28° K TIP = 300 x 10^{-6} c.g.s. unit

Correction for diamagnetism = 0.06 x 10^{-3} c.g.s. unit.

Lit. value [31] μ_{eff} = 5.04 B. M. θ = 30° K

Tables 15 - 19 contain the experimental results for the measurements of the compounds.

The values of μ_{eff}, θ, and TIP are summarized in table 20.

TABLE 20

Observed Magnetic Susceptibilities of $CoCl_2$ and its Hydrates

	μ eff	θ	TIP
$CoCl_2$	5.44	-19	0
$CoCl_2.H_2O$	5.16	3	0
$CoCl_2.2H_2O$	5.07	7	200×10^{-6}
$CoCl_2.4H_2O$	5.13	11	0
$CoCl_2.6H_2O$	4.98	28	300×10^{-6}

μeff is given in Bohr magnetons, θ in degrees K, and TIP in c.g.s. units.

Discussion

The magnetic moments for the cobalt chloride hydrates (μ_{eff} = 4.98 - 5.16 B. M.) are in the range expected for spin-free octahedrally coordinated cobalt (II) compounds[9]. Spin-free divalent cobalt has three unpaired electrons which would give a spin-only moment of 3.88 B. M. which is fairly independent of the environment of the ion as long as the

splitting of the d-shell does not become large enough to cause pairing of the electrons. The spin-only moment is found from the equation

$$\mu_{s.o.} = 4S\ (S + 1)^{1/2} \qquad (17)$$

where S is the spin quantum number.

The $^4T_{1g}$ ground state for cobalt(II) in an octahedral ligand field is called a magnetic orbital triplet meaning that it is a state where an orbital contribution to the magnetic moment is possible. If the configuration were tetrahedral, with an $^4A_2$ ground state, a smaller magnetic moment would be expected.

The value of 5.44 B. M. for $CoCl_2$ agrees fairly well with the value observed by Norman Elliott and others of 5.37 B. M. [10] The higher value for the susceptibility of $CoCl_2$ over the hydrates is in agreement with a more symmetrical octahedron with a near maximum orbital contribution to the moment. The lower values for the hydrates and the increasing value for θ with higher hydration agrees with the proposed higher distortions for the hydrated compounds.

CHAPTER VI

CONCLUSION

The crystal structures for $CoCl_2.6H_2O$,[11] $CoCl_2.2H_2O$,[12, 13] and $CoCl_2$[14] have been determined by x-ray analyses. These analyses can be used in conjunction with the thermodynamic values, spectra, and magnetic moments of each compound or dissociation step to determine the structural change during each dissociation step.

Cobalt chloride hexahydrate was shown by x-ray analysis to be octahedrally coordinated. The cobalt(II) ion is surrounded by four water molecules which lie in a slightly distorted square and two chloride ions which are trans with respect to each other. The octahedron is tetragonally distorted with the chloride ions at a greater distance from the cobalt ion than the water molecules. (Co-H_2O = 2.12 A, Co-Cl = 2.43 A) The remaining two moles of water lie outside of the inner coordination sphere and align and space the adjacent "squares" of coordinated water molecules. The non-coordinated water molecules link the adjacent "squares"

through hydrogen bonds and are in an ice-like environment. The third axis has a Co-Cl-Cl-Co configuration.

The first dissociation step involves the loss of two moles of water from the hexahydrate. The enthalpy change of 13.4 Kcal/mole of water is only slightly greater than the energy change necessary to change one mole of ice to the vapor phase at 30° C (approximately 12.4 Kcal/mole of water) and indicates that the first water molecules lost are the two moles of non-coordinated water. This helps explain why no pentahydrate is observed. The entropy change of 35.8 e.u./mole of water is approximately the same as the entropy change involved in changing one mole of ice to water vapor at 30° C (35.1 e.u./mole water) indicating little ordering in the crystal structure. The loss of the waters which align and space the cobalt units should result in some change, but it is difficult to predict the exact change, and the structure of the tetrahydrate has not been determined. There is almost no difference in the spectra of the tetrahydrate and hexahydrate indicating that the environment around the cobalt ion is virtually unchanged. The small difference in the magnetic moments of the two compounds also indicates that the ligand field surrounding the cobalt ion is unchanged. The slightly larger moment of the tetrahydrate

indicates a larger orbital contribution and slightly less distortion in agreement with the entropy change.

Two moles of water are lost from the tetrahydrate to form the dihydrate for which a crystalline structure has been determined by x-ray analysis. In the dihydrate which is also octahedrally coordinated, the central cobalt ion is surrounded by a square of four chloride ions and two water molecules trans to each other. As in the hexahydrate structure, the water molecules are closer to the central metal ion than are the chloride ions (Co-Cl = 2.45 and 2.48 A, Co-H_2O = 2.04 A). The two chloride ions on each side are shared by other cobalt ions and, therefore, form an infinite chain structure. The other axis is made up of a Co-H_2O-H_2O-Co unit which determines the spacing between octahedral units. When two water molecules are lost from the tetrahydrate, two chloride ions are moved in to replace them.

The relatively low enthalpy for the loss of water from the tetrahydrate (13.4 Kcal/mole H_2O) indicates the water molecules were bound with approximately the same strength as the non-coordinated water. The enthalpy change of 35.6 e.u./mole H_2O indicates that although considerable change must take place during the dehydration, the resulting dihydrate is very similar to the tetrahydrate in structure. Both have

tetragonal distortion as the major distortion, but the tetrahydrate has axial elongation, and the dihydrate has axial compression. The positive value of Ds for the tetrahydrate and negative value for the dihydrate is in agreement with this. The small values of Ds and Dt for the dihydrate indicate a slightly less distorted structure. The substitution of chloride ions for water molecules would be expected to produce a smaller value for Dq in agreement with the relative positions on the spectrochemical series. The change in Dq from 900 cm^{-1} to 850 cm^{-1} is in general agreement with the values calculated from the average field approximation (table 11), but both values are above the calculated values. The magnetic moments of the two compounds are almost identical and indicate very similar structures.

The enthalpy change is smaller for the loss of water from the dihydrate than for any other dissociation step (9.1 Kcal/mole H_2O). This may indicate that the Co-H_2O-H_2O-Co structure of the dihydrate is not stable, and the interaction between the waters may cause one water molecule to be "pushed" out of the crystal to give a more stable structure. Although the enthalpy change is small, the entropy change is large as shown by the change in the entropies of formation (table 5). The high entropy change corresponds to an increase

in the symmetry of the structure in agreement with the change in the spectra. The spectrum of the monohydrate is indicative of a more symmetric structure, more like that of the anhydrous compound. The value of Dq for the monohydrate (840 cm^{-1}) is only slightly lower than the value for the dihydrate. This and the more symmetrical structure indicate that the monohydrate structure is most probably composed of four chloride ions around the central metal ion and a $Co-H_2O-Co$ configuration on the third axis. The sharing of a water molecule lengthens the $Co-H_2O$ distance, reducing the effect of the water molecules and giving a less distorted structure than the dihydrate. This sharing of the water molecule would explain the more symmetrical spectrum and the value of Dq which is much larger than would be expected for the monohydrate if the cobalt ion were surrounded by five chloride ions and one water molecule. The magnetic moment of the monohydrate which is slightly larger than the dihydrate (5.16 vs. 5.07 B.M.) is in agreement with this picture.

The structure of anhydrous $CoCl_2$ has been shown by x-ray analysis to be the cadmium chloride structure where the cobalt ion is surrounded octahedrally by six chloride ions.[15] The structure is fairly symmetrical with very little distortion.

The enthalpy change for the loss of one mole of water from the monohydrate (18.0 Kcal/mole H_2O) is higher than for any other dehydration step. This may be explained by the proposed sharing of the water molecule by two cobalt ions. The entropy change is smaller for the reaction than any other reaction as shown by the changes in the entropies of formation. This is in agreement with the picture of a tightly bound molecule of water in a slightly distorted structure which is very close to the structure of anhydrous $CoCl_2$. The simple spectrum and high magnetic moment for the anhydrous compound indicate that it has the least distorted structure and that this gives the largest orbital contribution to the magnetic moment.

The three known structures ($CoCl_2.6H_2O$, $CoCl_2.2H_2O$, and $CoCl_2$) are all octahedral. The similarity of the magnetic moments and spectra of the other compounds indicate that they are also octahedral. The relatively low values for the entropy changes also indicate it very unlikely that a coordination number change occurs with the other compounds. (The value for ΔS^o for the loss of water from $(NH_4)_2Co(H_2O)_2Cl_4$ is 50 e.u./mole H_2O and the compound changes from octahedral to tetrahedral on dehydration.) Larger entropy changes would be necessary to switch from octahedral to tetrahedral and then reverse in so few steps.

PART II

DEHYDRATION OF POTASSIUM TETRACHLOROCOBALTATE(II) DIHYDRATE

CHAPTER VII

INTRODUCTION

Compounds containing the $CoCl_4^{--}$ ion have been studied by several different investigators during the last 50 - 60 years. The salts of all the alkali metals, ammonium ion and several of the alkaline earths have been prepared with the cesium salt receiving the most study. In the earlier years, the compounds were all written as double salts, but in the last few years as more knowledge of the structure has been gained, complex compounds have been determined, and a tetrahedral $CoCl_4^{--}$ unit has been found in each case.[17,18]

The potassium salt has been prepared by several investigators. Galuheva and Bergman prepared the salt but described it as a double salt, $CoCl_2.2KCl$.[19]

H. J. Seifert[20] prepared K_2CoCl_4 in a differential thermal analysis of the $KCl-CoCl_4$ system and found a congruent melting point of 436° C for the salt.

Wendlandt and Cathers proposed the formation of $CoCl_4^{--}$ ion in the final step of the dehydration of a $KCl-CoCl_2.6H_2O$

system.[21] The spectrum they obtained for the compound agrees with the spectrum obtained for K_2CoCl_4 as reported in chapter X.

Only a small amount of work has been done on K_2CoCl_4, and even less work has been done on its hydrate system.

CHAPTER VIII

PREPARATION OF SAMPLES

Potassium tetrachlorocobaltate(II) was prepared by dissolving stoichiometric amounts of KCl and $CoCl_2.6H_2O$ in concentrated hydrochloric acid and reducing the solution to dryness. The deep blue powder left behind was extracted with methanol several times. Residue from the extraction was discarded until the desired purity was reached as shown by analysis for the chloride ion; calculated Cl^- = 50.80 %, found 50.95 % ± .20 %. No more than two or three extractions were needed. The resulting blue material was heated in an oven at 150° C an additional six to eight hours.

The dihydrate and monohydrate were prepared by placing a weighed sample of the anhydrous compound in a desiccator over wet calcium nitrate until the desired weight gain was obtained. The hydration state was checked by dehydrating the hydrated samples. The amount of water lost was within 2 % of the theoretical value in each case.

CHAPTER IX

DISSOCIATION PRESSURES

Experimental

The dissociation pressures of potassium tetrachlorocobaltate(II) dihydrate and potassium tetrachlorocobaltate(II) monohydrate were measured with the apparatus and by the same methods discussed in chapter III for the hydrates of cobalt chloride. Part of the work was accomplished using a quartz spring with a load capacity of 0.5 grams and 0.40 - 0.45 gram samples, but most was done using a 1.0 gram load capacity quartz spring and samples of 0.7 - 0.8 grams.

The dissociation pressures were measured as a function of composition at constant temperatures of 54.5° and 40.0° C. The dissociation pressures of the dihydrate and monohydrate were also measured at constant composition as a function of temperature over the temperature range from 25° to 65° C. The results of both studies are shown in figures 14 and 15.

Figure 14 indicates that both moles of water are lost in a single dissociation step and at the same dissociation

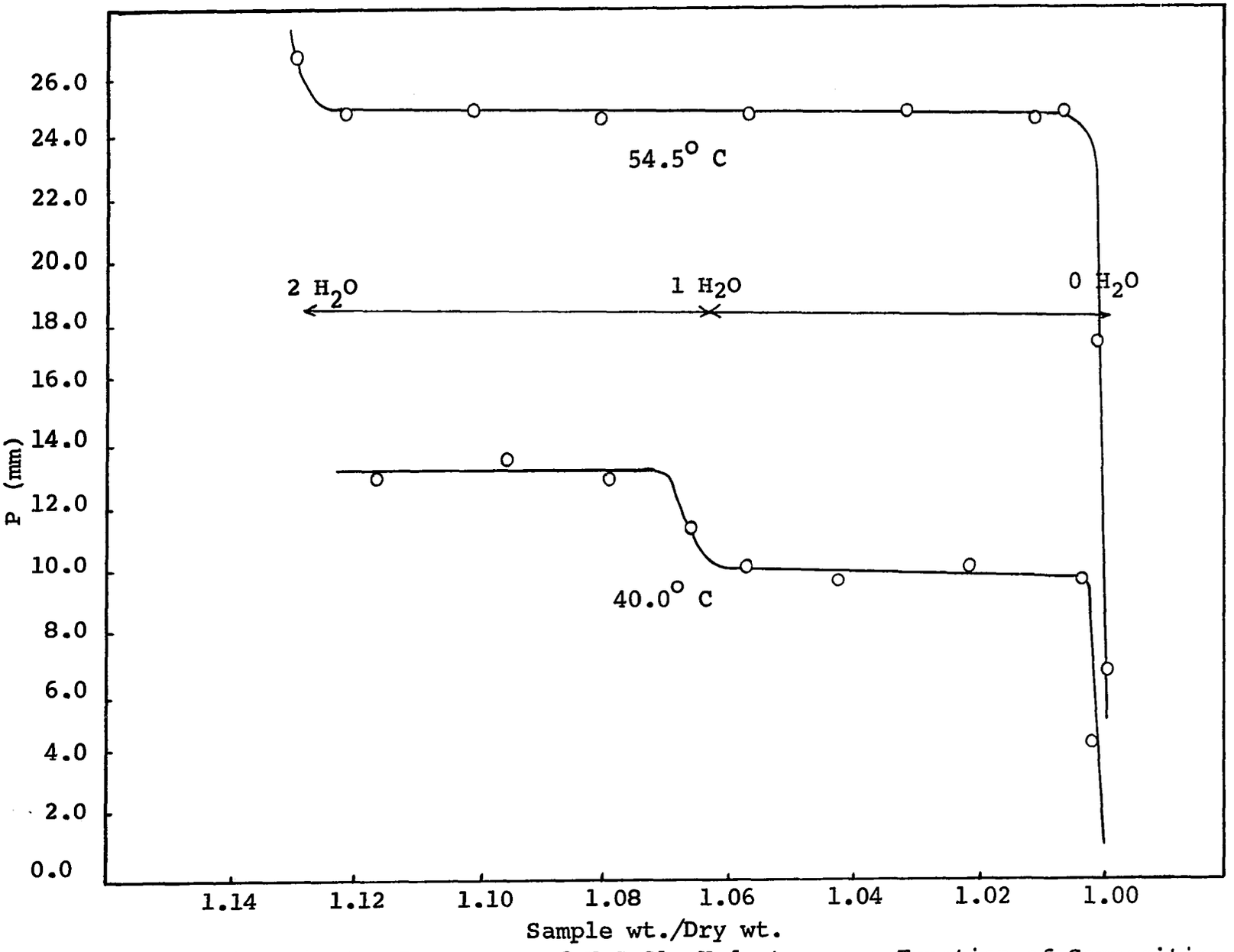


Figure 14 Dissociation Pressures of K_2CoCl_4 Hydrates as a Function of Composition

TABLE 21

DISSOCIATION PRESSURES

$K_2CoCl_4.2H_2O$ As A Function Of Composition

at 54.5° C	P (mm)	sample wt./dry wt.	moles H_2O
	26.3	1.127	1.97
	24.7	1.120	1.86
	24.9	1.102	1.58
	24.6	1.078	1.21
	24.7	1.055	0.85
	24.5	1.033	0.51
	24.0	1.013	0.20
	24.2	1.006	0.09
	17.1	1.003	0.05
	6.0	1.001	0.01
at 40.0° C	13.2	1.116	1.80
	13.5	1.096	1.49
	13.0	1.080	1.24
	11.1	1.066	1.04
	10.0	1.055	0.85
	9.4	1.042	0.65
	9.8	1.023	0.36
	9.0	1.005	0.08
	3.4	1.001	0.01

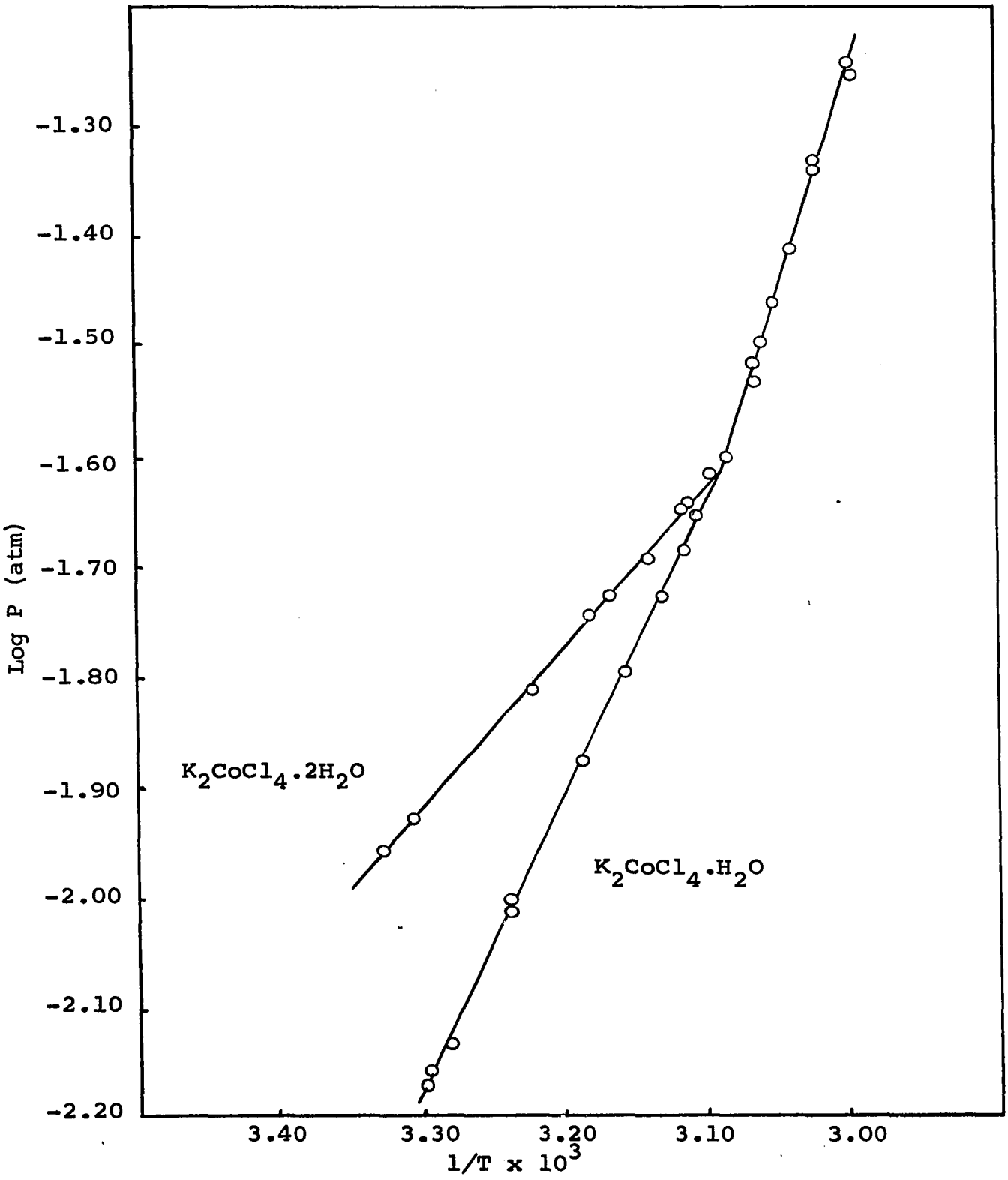


Figure 15 Dissociation Pressure of $K_2CoCl_4.2H_2O$ and $K_2CoCl_4.H_2O$ as a Function of Temperature

TABLE 22

DISSOCIATION PRESSURES

$K_2CoCl_4.2H_2O$ and $K_2CoCl_4.H_2O$ As a Function of Temperature

$K_2CoCl_4.2H_2O$

T °A	1/T x 10^3	P °C (mm)	Log P (atm)
300.2	3.331	8.1	-1.972
302.4	3.307	8.7	-1.941
308.4	3.243	10.9	-1.843
311.8	3.207	12.7	-1.777
313.6	3.188	13.2	-1.760
315.4	3.170	14.4	-1.722
320.9	3.116	17.6	-1.645
321.3	3.112	18.2	-1.621
325.8	3.069	22.8	-1.523
327.4	3.054	24.4	-1.476
329.4	3.036	29.2	-1.415
331.0	3.021	32.7	-1.366
334.7	2.988	41.8	-1.260

$K_2CoCl_4.H_2O$

303.0	3.300	5.0	-2.182
308.4	3.243	7.2	-2.024

TABLE 22 (continued)

$K_2CoCl_4.H_2O$

T ^oA	$1/T \times 10^3$	P ^oC	Log P (atm)
310.9	3.216	8.3	-1.962
313.2	3.193	9.6	-1.899
315.9	3.165	11.6	-1.816
318.4	3.141	13.4	-1.754
320.5	3.120	15.2	-1.699
320.9	3.116	16.4	-1.666
323.8	3.088	19.1	-1.600
326.4	3.063	23.3	-1.513
329.4	3.036	29.3	-1.414
331.0	3.021	32.3	-1.372
334.7	2.988	40.8	-1.270

pressure of 54.5° C. At 40° C two distinct dissociation steps are evident with the pressures dropping at the composition corresponding to the monohydrate. Figure 15 also shows the different dissociation pressures of the two dihydrates below 50° C which converge forming one straight line above 50° C.

This indicates that the monohydrate is formed as a distinct compound at temperatures below 50° C corresponding to the dehydration equations:

$$K_2CoCl_4.2H_2O_{(s)} = K_2CoCl_4.H_2O_{(s)} + H_2O_{(g)} \qquad (18)$$

$$K_2CoCl_4.H_2O_{(s)} = K_2CoCl_{4(s)} + H_2O_{(g)} \qquad (19)$$

Above 50° C both moles of water are removed in a single step corresponding to the equation:

$$K_2CoCl_4.2H_2O_{(s)} = K_2CoCl_{4(s)} + 2H_2O_{(g)} \qquad (20)$$

Calculations

In the same method as used for the hydrates of cobalt chloride, the variation in dissociation pressure with temperature for each dissociation step was fitted to the equation

$$\text{Log } P = - \Delta H^\circ/2.303\ nRT + \Delta S^\circ/2.303\ nR \qquad (5)$$

when P is the pressure in atmospheres, T is the absolute temperature, ΔH° and ΔS° are respectively the standard

enthalpy and entropy for the reactions, and n is the number of moles of water lost in the dissociation step.

Log P for each of the dissociation reactions below 50° C and the single step reaction above 50° C was plotted against 1/T with the slopes of the straight lines obtained equal to $-\Delta H^{\circ}/2.303\ nR$. The standard free energy, ΔF°, of each reaction at 30° C was calculated from the equation

$$\Delta F^{\circ} = -2.303\ nRT \log P. \qquad (6)$$

The standard entropy, ΔS°, was found for each reaction from the standard enthalpy and free energy by the relationship

$$\Delta S^{\circ} = \frac{\Delta H^{\circ} - \Delta F^{\circ}}{T} \qquad (7)$$

The thermodynamic constants obtained are given in table 23.

Discussion

Below 50° C the hydrated water is lost from the dihydrate in two dissociation steps. The first mole of water lost from the dihydrate is relatively weakly bonded and is lost with an enthalpy change of 6.96 Kcal/mole. However, the low value for ΔS° of 14.2 e.u. indicates a major change in the crystal structure with greater ordering in the monohydrate (see chapter III). The entropy change is smaller than any step in the cobalt chloride system which appears to be octahedral throughout.

TABLE 23

Thermodynamic Constants For The Dehydration Reactions

Of The K_2CoCl_4 Hydrates at 30° C

Below 50° C	ΔH° cal/ mole	ΔF° cal/ mole	ΔS° e.u./ mole
$K_2CoCl_4.2H_2O_{(s)} = K_2CoCl_4.H_2O_{(s)} + H_2O_{(g)}$	6,960	2,670	14.2
$K_2CoCl_4.H_2O_{(s)} = K_2CoCl_{4(s)} + H_2O_{(g)}$	12,710	3,020	32.0
Above 50°			
$K_2CoCl_4.2H_2O_{(s)} = K_2CoCl_{4(s)} + 2H_2O_{(g)}$	29,840	6,310	77.6

The energy required to remove the remaining mole of water from the monohydrate is 12.71 Kcal. This is considerably higher than the enthalpy change for the loss of the first mole of water and is almost equal to the energy required to change one mole of ice to water vapor at 30° C (12.4 Kcal/mole). The entropy change of 32.0 e.u. is closer to the value for changing ice to water vapor at the same temperature (35.1 e.u./mole) and indicates a much smaller change in the crystal structure than the loss of the first water.

A sealed glass container filled with the dihydrate was placed in an oven and studied at a series of temperatures above 50° C. At temperatures up to 70° C the violet sample appeared to change colors slightly toward a blue, and at temperatures above 100° C a phase change was observed giving a dark blue semi-solid.

The enthalpy change for the reaction above 50° C is 29.84 Kcal/mole. This is greater than the sum of the enthalpy changes for the individual reactions below 50° C (19.67 Kcal) by approximately 10 Kcal. A change in phase, which would require energy, will explain the 10 Kcal difference between the enthalpy changes above and below 50° C. The entropy change above 50° C is 77.6 e.u., and this is also explained on the basis of a proposed phase change.

CHAPTER X

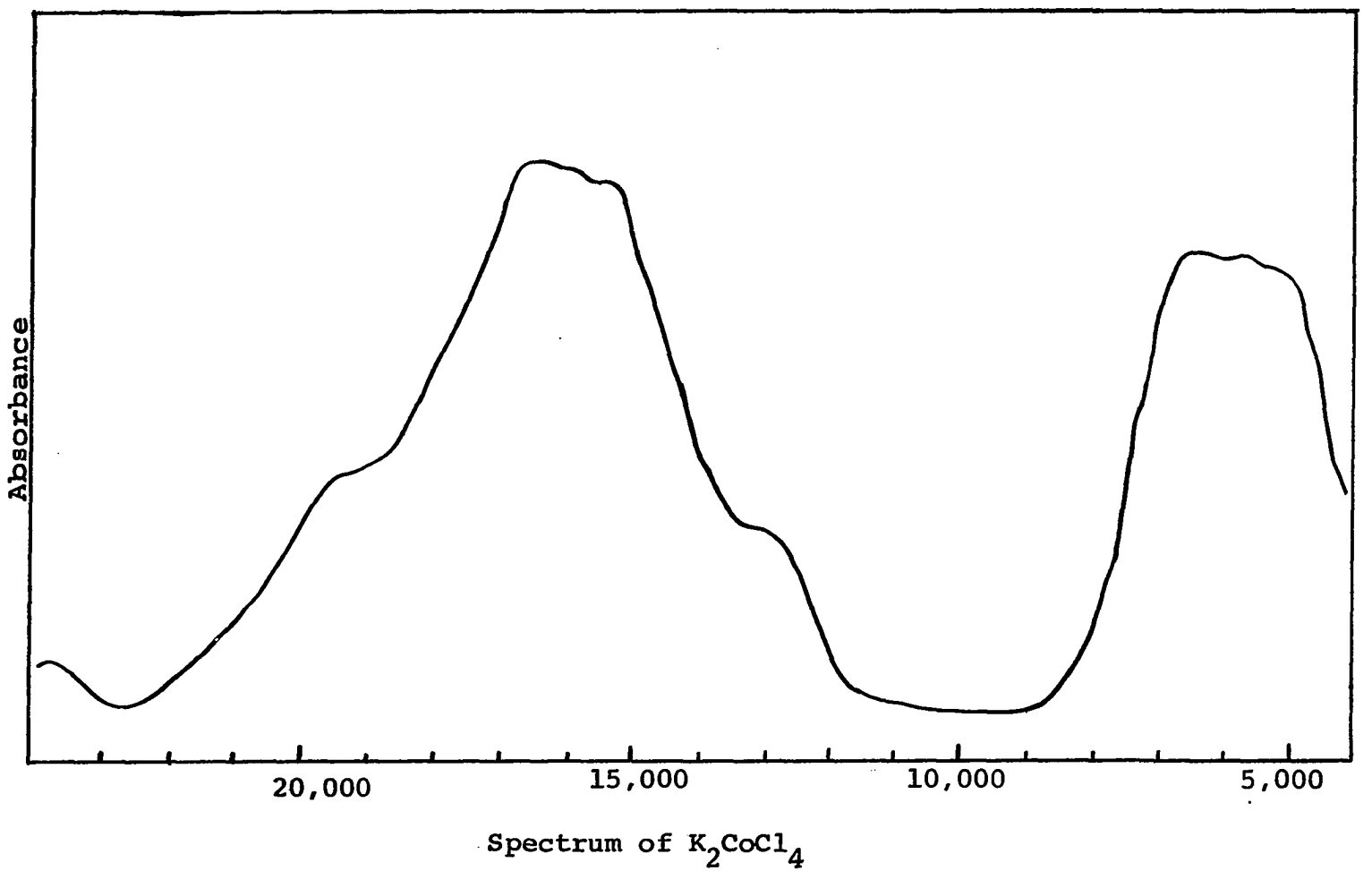
SPECTRA

Experimental

Samples of K_2CoCl_4, $K_2CoCl_4.H_2O$, and $K_2CoCl_4.2H_2O$ were prepared by methods discussed in chapter VIII. The samples were placed in the depression in a glass slide and sealed with a thin cover plate. The spectra were measured on a Beckman Model DK-1 double beam recording spectrophotometer equipped with a reflectance attachment for measuring solid samples. The spectrum of each compound was measured at least twice with different samples and very close agreement was obtained in each case.

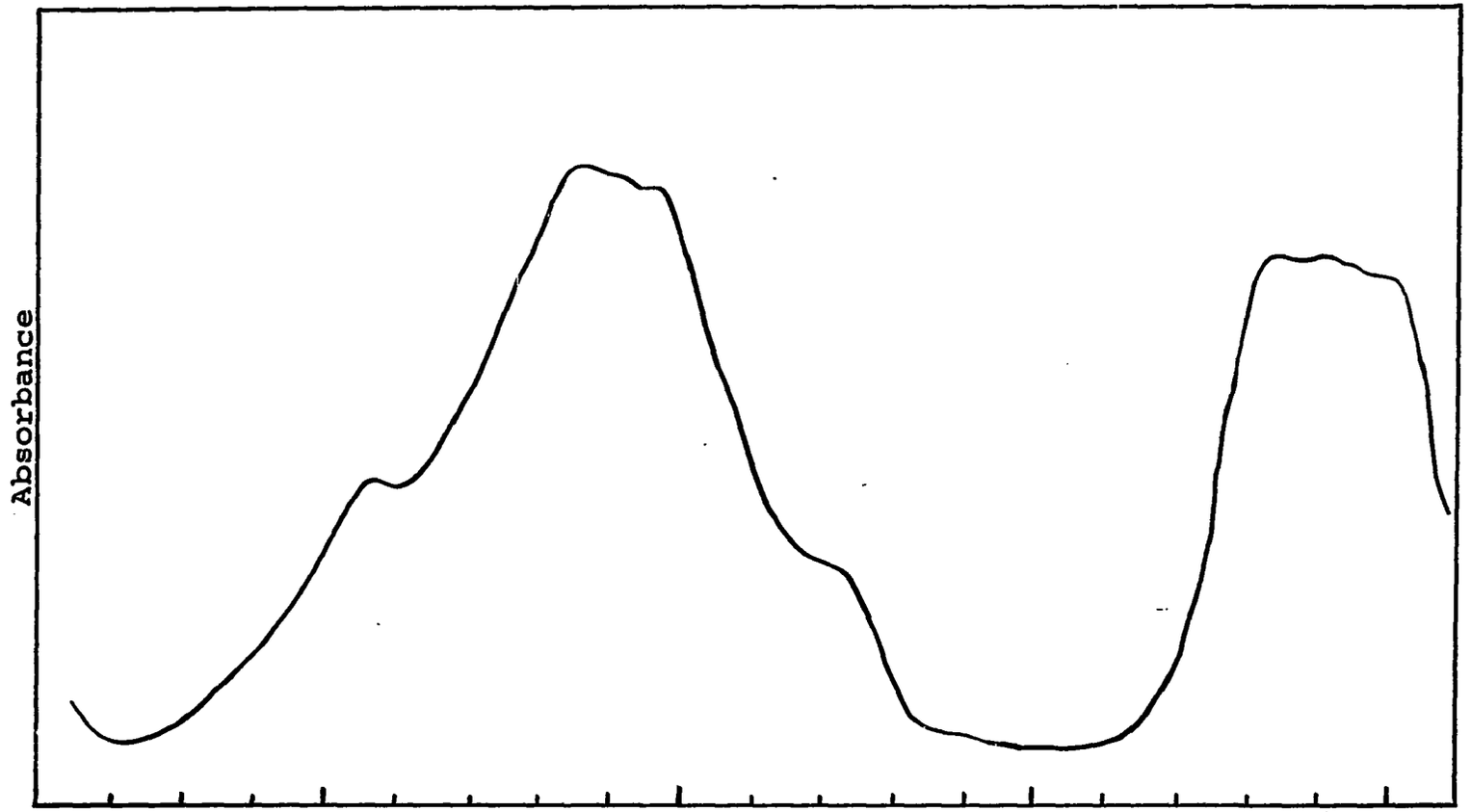
In an effort to determine the changes in the dihydrate at higher temperatures, a sample of dihydrate in the sealed sample chamber was heated in an oven at several temperatures above 50° C, and the spectrum of the hot sample was quickly measured. It was necessary to reheat the sample several times, taking only a portion of the spectrum each time until the entire spectrum was obtained.

The spectra are recorded in figures 16 - 18.



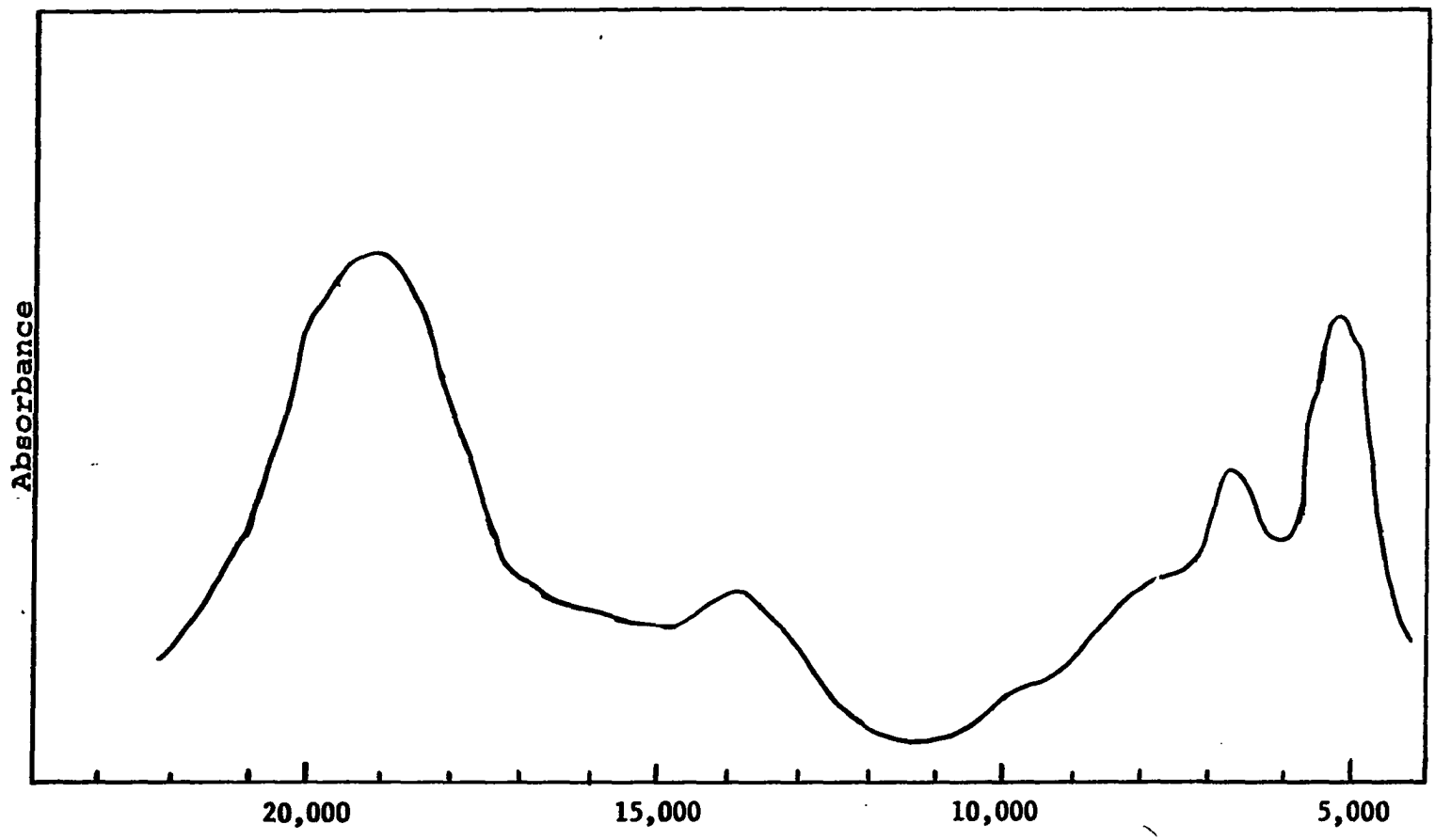
Spectrum of K_2CoCl_4

Figure 16



Spectrum of $K_2CoCl_4.H_2O$

Figure 17



Spectrum of $K_2CoCl_4.2H_2O$

Figure 18

Calculations

The spectrum of K_2CoCl_4 is complex and is composed of two main bands, one in the near infrared region and the other in the visible region. Although the absorptivity is given in relative values, the intensity of the peaks in the spectra of the anhydrous and monohydrate compounds is much greater than the intensity of the dihydrate spectrum. The spectrum of potassium tetrachlorocobaltate(II) was found to be very similar to the spectrum observed for ammonium tetrachlorocobaltate(II)[16]. Each contains a broad band in the visible region which is characteristic of the tetrahedral Co(II) complexes. The monohydrate spectrum is almost identical to the anhydrous compound indicating that the two compounds have the same coordination. The dihydrate is different from the other two compounds indicating that it has a different structure, probably a different coordination number.

The energy level diagram for octahedral d^7 compounds is given in figure 10. The energy level diagram for a tetrahedral d^7 compound is found by inverting the diagram for octahedral compounds. In both cases three bands would be expected for a non-distorted compound, and several extra bands would be expected for tetragonal distortion.

The spectrum of $K_2CoCl_4.2H_2O$ was almost identical to that of $CoCl_2.2H_2O$, and it was fitted to distortion equations assuming a tetragonally distorted octahedral configuration. The best fit was obtained with the values of Dq = 845 cm^{-1}, Ds = -220 cm^{-1}, and Dt = 110 cm^{-1}. A transition to the excited ^2G energy level is possible between the first and second transitions of a weak field octahedral d^7 compound. Although the exact energy of the absorption could not be calculated, the band at 7900 cm^{-1} is tentatively assigned to the transition to the ^2G state.

The crystal field splitting parameter, Δ, for a tetrahedral compound can be calculated from the value of Δ for an octahedral compound with the same central metal ion and ligands at the same distances through the equation

$$\Delta_{tetra.} = 4/9\ \Delta_{oct.} \qquad (21)$$

Using 7500 cm^{-1} for Δ oct from the $CoCl_2$ spectrum, the expected value for Δtetra is 3330 cm^{-1}. The first transition, equal to 10 Dq, would be expected in the infrared region of the spectrum. The infrared spectrum of a pressed KBr pellet containing K_2CoCl_4 was measured, but no absorption was found. However, the transition from $^4A_2$ to $^4T_2$ is symmetry forbidden, and only a small peak, if any, would be expected. The large band in the near-infrared

region was assigned to the second transition of the anhydrous compound, and the complex band in the visible region was assigned to the third transition in agreement with the assignment made by Wendlandt and Cathers[21] and others[22,23]. The best value obtained for Dq was 335 cm^{-1}.

An attempt was made to fit the spectrum of the anhydrous compound assuming tetragonal distortion, but a good fit was not obtained. The complex spectrum indicated distortion of some type which may be trigonal or rhombic. However, no attempt was made to consider either type.

The spectrum of the monohydrate was almost identical to that of the anhydrous compound. Its spectrum was also fitted considering a tetrahedral configuration with the same value for Dq as found for the anhydrous compound.

The calculated and observed values for the absorption peaks are given in tables 28, 29, and 30.

Discussion

The bands in the visible region of the anhydrous and monohydrate spectra agree very closely with the reported spectra of other cobalt(II) compounds known to be tetrahedral[24,25]. This agreement together with the fitting of the spectra lead to the conclusion that K_2CoCl_4 and $K_2CoCl_4 \cdot H_2O$ are both tetrahedral compounds. Distortion, other than

TABLE 24

Spectrum of K_2CoCl_4

	Observed Center of Band	Description	Calculated
			2,680
1.	4,820	Broad, nearly flat band, Fairly high intensity; Possible to separate into five peaks	
	5,570		
	5,820		6,030
	6,490		
	6,850		
2.	12,740	Low intensity peak	
3.	15,280	Very high intensity complex band; possible to resolve into four peaks	
	15,880		
	16,950		16,510
	19,240		

All values reported in cm^{-1}

Dq = 335 cm^{-1}

TABLE 25

Spectrum Of $K_2CoCl_4.H_2O$

	Observed Center of Band	Description	Calculated
			2,680
1.	4,860	Broad, nearly flat band, fairly high intensity; Possible to separate into six peaks	
	5,190		
	5,560		
	5,800		6,030
	6,540		
	6,940		
2.	12,820	Low intensity peak	
3.	15,170	Very high intensity complex band; possible to separate into four peaks	16,510
	15,620		
	16,670		
	19,230		

All values reported in cm^{-1}

Dq = 335 cm^{-1}

TABLE 26

Spectrum Of $K_2CoCl_4.2H_2O$

	Observed Center of Band	Description	Calculated
1.	5,190	Sharp, fairly intense peak	5,154
2.	5,620	Weak, unsymmetrical peak	5,580
	5,820	Composed of two peaks	5,830
3.	6,990	Fairly broad, unsymmetrical band	6,793
4.	7,900	Low, broad peak	
5.	12,740	Low intensity peaks	13,604
	14,190		14,280
6.	16,950	Broad, complex band; Possible to separate into five individual peaks	18,118
	18,870		18,794
	19,410		19,042
	20,000		19,718
	21,750		

All values reported in cm^{-1}

Dq = 845 cm^{-1}

Ds = -220 cm^{-1}

Dt = 110 cm^{-1}

tetragonal, appears to be present, but the exact type was not determined.

The fitting of the $K_2CoCl_4.2H_2O$ spectrum and its close resemblance to that of $CoCl_2.2H_2O$ indicate that it is octahedrally coordinated with tetragonal distortion as its major distortion. Although its spectrum could be fitted with a positive Ds (axial elongation) or a negative Ds (axial compression), the negative value for Ds gave the better fit. The exact structure is not known, but it is probable that the water molecules are trans to each other and closer to the cobalt ion than the chloride ions analogous to $CoCl_2.2H_2O$.

CHAPTER XI

MAGNETIC SUSCEPTIBILITIES

Experimental

Samples of K_2CoCl_4, $K_2CoCl_4.H_2O$, and $K_2CoCl_4.2H_2O$ were prepared by methods discussed in chapter VIII. The magnetic susceptibility of each compound was measured with the magnetic balance described in chapter V. The susceptibility was measured over the temperature range 77° to 300° K with sample size from 0.04 gram to 0.07 gram. Liquid nitrogen and mixtures of acetone-dry ice, alcohol-ice, and water-ice were used in the low temperature range. Some measurements were made by placing liquid nitrogen in the Dewar flask around the sample and measuring the susceptibility as the liquid nitrogen evaporated and the temperature rose. At each temperature the maximum deflection up and down in the magnetic field was measured with a cathetometer.

Calculations

The susceptibility per gram, χg, and the molar susceptibility, χ_M, for each compound at each temperature were

calculated from equations 11 and 12 (page 45). The compounds were found to obey the Curie-Weiss law (equations 13 and 14). T vs $1/\chi_M$ was plotted with the Weiss constant, θ, taken as the intercept on the T axis. A plot of χ_M vs $\frac{1}{T + \theta}$ was made, and the temperature independent paramagnetism (TIP) was found as the intercept on the χ_M axis and the Curie constant from the slope in accordance with the equation:

$$\chi_M = \frac{C_M}{T + \theta} + TIP \qquad (15)$$

The effective magnetic moment, μ_{eff}, was calculated in each case from the Curie constant from the relationship:

$$C_M = 1/8\ \mu^2_{eff} . \qquad (16)$$

The values obtained for μ_{eff}, and TIP for each compound are given in table 27.

TABLE 27

Magnetic Susceptibilities of K_2CoCl_4, $K_2CoCl_4.H_2O$, and $K_2CoCl_4.2H_2O$

	μ_{eff}	θ	TIP
K_2CoCl_4	4.85 B.M.	15° K	400×10^{-6} c.g.s. unit
$K_2CoCl_4.H_2O$	4.87 B.M.	10° K	250×10^{-6} c.g.s. unit
$K_2CoCl_4.2H_2O$	5.22 B.M.	10° K	300×10^{-6} c.g.s. unit

The molar susceptibilities at each temperature for the three compounds are given in tables 28 - 30. The diamagnetic correction for each compound is -136×10^{-6} c.g.s. unit.

TABLE 28

Observed Magnetic Susceptibilities (in units of 10^{-3} c.g.s. - e.m.u. per mole) of K_2CoCl_4

T ^{o}K	χ_M (corrected)
293	9.70
198	14.14
179	15.47
141	19.27
77	32.45

μ_{eff} = 4.85 B.M.

θ = 15^{o} K

TIP = 400 x 10^{-6}

TABLE 29

Observed Magnetic Susceptibilities (in units of 10^{-3} c.g.s. - e.m.u. per mole) of $K_2CoCl_4.H_2O$

T ^oK	χ_M (corrected)
290	10.09
251	11.76
201	14.10
176	16.42
77	34.51

μ_{eff} = 4.87 B.M.

$\theta = 10^o$ K

TIP = 250 x 10^{-6}

TABLE 30

Observed Magnetic Susceptibilities (in units of 10^{-3} c.g.s. - e.m.u. per mole) of $K_2CoCl_4.2H_2O$

T ^{o}K	χ_M (corrected)
301	11.73
273	12.25
263	12.92
201	16.20
124	25.83
77	39.51

μ_{eff} = 5.22 B.M.

$\theta = 10^{o}$ K

TIP = 300×10^{-6}

Discussion

The magnetic moments for K_2CoCl_4 and $K_2CoCl_4.H_2O$ of 4.85 B.M. and 4.87 B.M. are in the upper range expected for tetrahedral compounds of divalent cobalt. (Equation 22 indicates values between 4.4 and 4.8 B.M.[26]; Observed; Cs_3CoCl_5 4.62 B.M.[27]; $(Ph)_4As[CoCl_4]$ 4.71 B.M.[28]; $K_2Co(CNS)_4.4H_2O$ 4.47 B.M.[29]). It is highly unlikely that such a small change in susceptibility could accompany a major change in configuration. This is in agreement with the spectra for a tetragonal configuration for both compounds.

Although an appreciable orbital contribution to the susceptibility is not expected in tetrahedral Co^{+2} compounds, spin-orbit coupling of the ion is able to "mix in" some of the higher levels with orbital angular momentum[30]. The magnitude of this effect can be approximated with the relationship

$$\mu_{eff} = \mu_{s.o.} \left(1 - \frac{\alpha \lambda}{\Delta}\right) \qquad (22)$$

where $\mu_{s.o.}$, the spin only moment is 3.89 B.M., α is a constant equal to 4 in this case, λ is the spin-orbit coupling constant, and Δ is the crystal field splitting parameter equal to 3350 cm^{-1}. If the spin-orbit coupling constant is calculated using 4.85 B.M. for μ_{eff}, the value

found is -206 cm^{-1}. This is above the value found for the free ion (-177 cm^{-1}) and may be indicative of distortion which splits the $^4T_{2g}$ and $^4T_{1g}$. If strong distortion is present, splitting of the $^4T_{2g}(F)$ may be so large that equation 22 is no longer applicable.

The susceptibility for the dihydrate of 5.22 B.M. is above the maximum values expected for a tetrahedral compound, but in the range expected of an octahedral compound. The large change in the magnetic moment indicates a major change in the electronic structure and a different ground state than was observed in the anhydrous and monohydrate compounds.

CHAPTER XII

CONCLUSION

The spectra and high magnetic susceptibility of $K_2CoCl_4.2H_2O$ show very strongly that it is octahedrally coordinated and probably should be expressed as $K_2Co(H_2O)_2Cl_4$. The ground state of the octahedrally coordinated cobalt ion is $^4T_{1g}$, and the spectra gave the best fit considering axial compression with a negative value for Ds. Other types of distortion may be present such as trigonal or rhombic, but if so, they appear to be minor compared to the tegragonal distortion.

Vapor pressure work showed that at temperatures below 50^o C one mole of water is lost from the dihydrate with a major change in structure as indicated by the low value for the entropy change. The accompanying decrease in magnetic susceptibility and the change in spectra indicate that the best explanation is a change from a distorted octahedral to a distorted tetrahedral structure. The type of distortion

present in the monohydrate was not determined, but the spectrum indicated that it is not tetragonal.

The second mole of water is lost below 50° C giving the anhydrous compound, K_2CoCl_4. An entropy change close to that for the transfer of the water to the vapor phase indicated a relatively small change in the solid phase. The spectra and magnetic moments of the monohydrate and anhydrous compounds are in agreement with the thermodynamics in the similarity of the two compounds. It was also observed that while the dihydrate is violet, the monohydrate and anhydrous compounds are both deep blue. This would indicate that the $CoCl_4^{=}$ anion is present in both cases, although this cannot be stated with certainty.

Above 50° C the vapor pressures of the dihydrate and monohydrate were found to be identical. Both moles of water were lost in a single dissociation step as shown in figure 14.

The large enthalpy and entropy changes above 50° C and the change in the spectrum of the dihydrate are best explained by phase and structural changes probably involving a polymeric structure which begin at 50° C and lead to a tetrahedrally coordinated compound at temperatures over 100° C.

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APPENDIX

During the vapor pressure work, it was observed that at temperatures above 52° C, the cobalt chloride hexahydrate melted to a dark blue semi-solid and at higher temperatures, melted into a dark blue liquid. The color change indicated a possible coordination change; so farther work was carried out on the hexahydrate at higher temperatures.

The spectrum of the hexahydrate was measured at higher temperatures by heating a sample in a sealed container to a temperature sufficient to produce the dark blue semi-solid and quickly measuring a portion of the spectrum. When the sample resolidified, the procedure was repeated until the complete spectrum was obtained. The visible band was shifted toward lower energy from that observed at lower temperatures and gave the characteristic high intensity peaks of the tetra-chlorocobaltate(II) ion as was found with K_2CoCl_4. A broad band at 5600 - 6800 cm^{-1} was also observed which was found in the spectrum of K_2CoCl_4 but was not present in the spectrum of the hexahydrate at lower temperatures.

An attempt was made to determine the magnetic susceptibility of the hexahydrate at steam temperatures. Three separate measurements were made, but good agreement was not obtained due to the rapid dehydration of the hexahydrate. The values for μ_{eff} obtained varied from 4.3 - 4.7 B. M., well below that determined for the hexahydrate as would be expected if the tetrahedral ion were formed.

Although this work was not completed, the color change, change in spectrum, and magnetic susceptibility indicate octahedral cobalt chloride hexahydrate forms a dark blue tetrahedral complex when the hexahydrate is heated above 52^{o} C.